Thermodynamics
&
Statistical Physics

for

CSIR-UGC-NET/JRF|GATE
TIFR | JEST | BARC | IISc | JNU | SLET | Ph.D Entrance

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PREFACE

The present booklet on Thermodynamics and Statistical Physics section of the Physical Sciences deals with the syllabi mentioned in the CSIR & GATE in their respective notifications. The Booklet has been designed and organised in a manner so that the aspirants can make full use of it for their immaculate preparation.

The panel of experts and faculties in the R&D team of Career Endeavour have done lots of hard work and that too with immense care in formulating the booklet into its present form. A brief discussion is given on every topic mentioned in syllabus along with ample of solved examples on the concepts discussed. The idea is not only to bring out the basic concepts clearly but also to help the students in developing the analytical approach for solving any problem.

The booklet contains 96 descriptive solved examples in addition to around 100 objective problems that have appeared in GATE sometimes. The GATE problems are numbered with 'G' and distributed topic wise for the help of the students. It is expected that the booklet will form an integral part of the Classroom/Correspondence program which the student would join for his/her success at Career Endeavour. Even though due care has been taken while preparing the booklet, the booklet may contain errors/mistakes here and there, we sincerely apologize for the same. We would be also thankful to those readers who point out the errors.

Finally, we from the R&D team of Career Endeavour, wish all the aspirants 'GOOD LUCK' and will always be available to help them out so that they come up with 'flying colors'.

THANK YOU

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Chapter 1

Basic Introduction

Thermodynamics :
This is the branch of Physics in which we deal with **internal macroscopic state of the system.**

System : Any portion of matter which is considered as **separated from its surrounding** is called system.

Surrounding : All these things which are outside the system and influence its behaviour are known as surrounding.

Example : Let a gas be filled in a cylinder fitted with a piston heated by a burner. Here the gas is the system while the piston and burner are the sorroundings.

Thermodynamic system : A thermodynamic system is one which may interact with its sorrounding in atleast two distinct ways and one of these necessarily a transfer of heat(In or out of the system) and the other may be some other means of transfer of energy say be performance of mechanical work by or on the system through electromagnetic interaction.

Example: Gas contained in a cylinder, vapour in contact with its liquid stretched wire.

Equilibrium : If there is no change in the property of the system w.r.t. time, the system is called in equilibrium.

1. **Mechanical equilibrium :** When there is no unbalanced force interior of the system and between the system and surrounding then the system is in mechanical equilibrium.
Example: Ideal gas inside a container.

2. **Chemical equilibrium :** If the system has no tendency to undergo a change in internal structure and also has no tendency to transfer matter from one part to another part then it is said to be in chemical equilibrium.

3. **Thermal equilibrium:** If there is no temperature difference between any part of the system and also not between the system & surrounding then the system is in thermal equilibrium.

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4. **Thermodynamic equilibrium:** A system is said to be in thermodynamical equilibrium if its state doesn't change in any way i.e. mechanical chemical & thermal equilibrium.

If however the conditions for any one of three type of equilibrium are not satisfied then the system is said to be in non thermodynamic equilibrium. If all are not satisfied then system is called in non-equilibrium.

Microscopic parameter : The parameter of the order of atomic level is called microscopic parameter. There are parameters that describes the internal structure of the system or associated with the constituent of the system. These parameters can't be directly measured in laboratory and can't be experience by our sense of perception.
Example: mass, velocity, energy, momenta, magnetic moment of constituent (atom or molecule) of the system.

Macroscopic parameter: Macroscopic parameter of a system are the average of the sum total of the corresponding microscopic parameter of the constituent particles. These can be measured directly in the laboratory and can be directly experienced by our sense of perception.
Example: pressure, volume, temperature, entropy

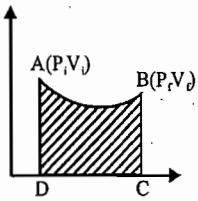
Microstate: The state of the system associated with the states of all constituents of the system is called microstate or microscopic state.

Macroscopic State : The state of the system associated with the parameters of the whole system is called macrostate. The macrostate is called thermodynamic state.

A thermodynamic system is taken from initial to final state the work done by the system is given by

$$dW = FdS = PAdS = PdV$$

$$W = \int_{\text{initial}}^{\text{final}} dW = \int_{i}^{f} PdV$$



work done on the system is – ve

work done by the system is + ve

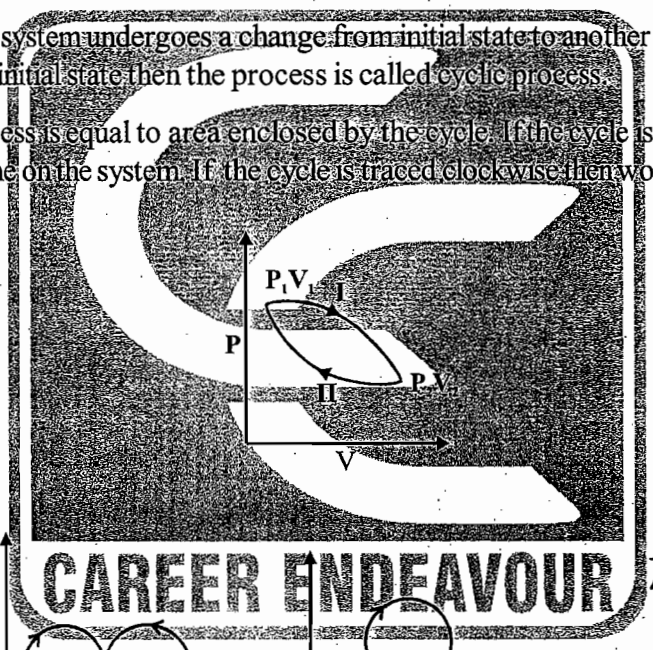
work done = Area under the curve (on PV diagram)

work done depends on the path and can't be written as perfect differential similarly heat also depend on path and can't be written as perfect differential.

P, V, T, U, S are exact or perfect differential (state or point function)

Cyclic Process : When a system undergoes a change from initial state to another final state through different states and come back to initial state then the process is called cyclic process.

Work done in cyclic process is equal to area enclosed by the cycle. If the cycle is traced anticlockwise work done is –ve i.e. work done on the system. If the cycle is traced clockwise then workdone is +ve i.e work done by the system.



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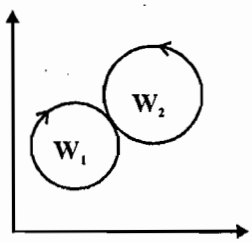


$W_1 < W_2$ $W = W_2 - W_1$

W_2 is anticlockwise

W_1 is clockwise

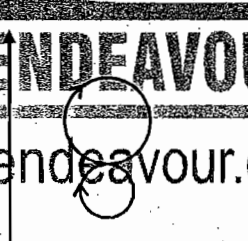
So work done on the system

$W = W_1 + W_2$

W_1 is clockwise

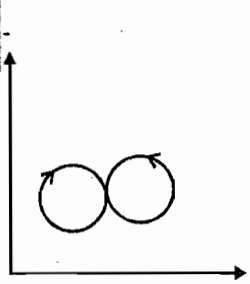
W_2 is anticlockwise

So work done by the system



$W = W_1 + W_2$

W_1 is clockwise and W_2 also work done by the system



$W_1 = W_2$

work done is zero

Internal energy : The internal energy is the energy associated with microscopic mechanical energy

I .E = K.E + P . E

It is impossible to divide internal energy into a a thermal and mechanical part

Let Q be the heat absorbed by the system and W be the work done by the system during the process that leads the system from initial state to final state Q – W is calculated then Q – W is same for different path although Q & W individually are different for different path. Then this is called change in internal energy dU.

$$dU = Q - W$$

Q – W depend only on state (initial & final) and not on the path the internal energy of a system in a given state is a function of that state only and doesn't at all depend upon the way by which that state has been acquired

Hence we can't tell weather the internal energy of the system has been acquired by heat transfered or by performance of mechanical work or by both.

The Kinetic Theory of Gases

We can summarize the kinetic theory of gases with four basic postulates:

1. **Gases are made up of molecules:** We can treat molecules as point masses that are perfect spheres. Molecules in a gas are very far apart, so that the space between each individual molecule is many orders of magnitude greater than the diameter of the molecule.

2. **Molecules are in constant random motion:** There is no general pattern governing either the magnitude or direction of the velocity of the molecules in a gas. At any given time, molecules are moving in many different directions at many different speeds.

3. **The movement of molecules is governed by Newton's Laws:** In accordance with Newton's First Law, each molecule moves in a straight line at a steady velocity, not interacting with any of the other molecules except in a collision. In a collision, molecules exert equal and opposite forces on one another.

4. **Molecular collisions are perfectly elastic:** Molecules do not lose any kinetic energy when they collide with one another.

The kinetic theory projects a picture of gases as tiny balls that bounce off one another whenever they come into contact. This is, of course, only an approximation, but it turns out to be a remarkably accurate approximation for how gases behave in the real world. These assumptions allow us to build definitions of temperature and pressure that are based on the mass movement of molecules.

- **Gas Laws**
  Boyles Law : PV = constant
  Charles Law : V/T = constant
- **Ideal Gas Equation**
  PV = nRT
- **Dalton Law of Partial Pressure**
  $P = P_1 + P_2 + P_3$
  Pressure exerted by n moles of an ideal gas in terms of the speed of the molecules

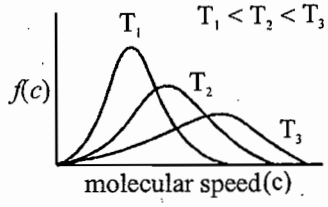
$$p = \frac{nM(v_{rms})^2}{3V}$$

- **Kinetic Theory of gases:**
  The number of particle moving with velocity c and c + dc is given by

$$dN_c = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2k_B T}} c^2 dc$$

where N is the total number of gas particles and

$$f(c) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2$$ is called Maxwell's distribution function.



Average speed, r.m.s speed and most probable speed:

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Average speed : $\bar{c} = \frac{1}{N}\int_0^{\alpha} c dN_c = \sqrt{\frac{8k_BT}{\pi m}}$

R.M.S speed : $c_{rms} = \sqrt{\frac{1}{N}\int_0^{\alpha} c dN_c} = \sqrt{\frac{3k_BT}{m}}$

Most probable speed:

$$\left.\frac{df}{dc}\right|_{c=c_m} = 0$$

We get $c_m = \sqrt{\frac{2k_BT}{m}}$

$$\bar{c} : c_{rms} : c_m = \sqrt{\frac{8k_BT}{\pi m}} : \sqrt{\frac{3k_BT}{m}} : \sqrt{\frac{2k_BT}{m}}$$

$$\Rightarrow \boxed{c_m : \bar{c} : c_{rms} = 1 : 1.128 : 1.224}$$

Maxwell's distribution function in momentum and energy form:

The number of particles moving with energy E and $E + dE$ is given by

$$dN_E = 2N\left(\frac{E}{\pi}\right)^{1/2}(k_BT)^{-3/2}e^{-E/k_BT}dE$$

The number of particle moving momentum p and dp is given by

$$dN_P = 4\pi N\left(\frac{1}{2\pi mk_BT}\right)^{3/2}e^{-\frac{p^2}{2mk_BT}}p^2dp$$

- **Degree of freedom:**

The degree of freedom of a dynamical system may be defined as the total number of independent co-ordinates require to specify its position and configuration. Thus degree of freedom indicates the total number of independent direction in which a particle can move.

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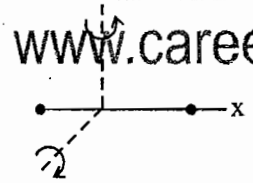
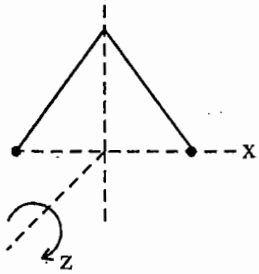
N_2, O_2, N_2



Diatomic molecular

The molecule can structured along z-axis, rotate along z-axis and can rotate about at its position. Thus total number of degree of freedom = 5

y CO_2, O_3, CH_4



Triatomic Molecule

It can structured and rotate along all the three axis thus total number of degree of freedom = 6

Law of equipartition of energy:

It states that for any given thermodynamical system with n degree of freedom, the K.E. associated with each degree of freedom is given by $\frac{1}{2}k_BT$. Where k_B is Boltzmann constant and T is the absolute terms.

Maxwell velocity distribution for one dimension.

$$F(v) = N\left(\frac{M}{2\pi k_BT}\right)^{1/2} e^{\frac{-E_q}{2k_BT}} dv$$

But from the assumption of kinetic theory we know that molecules posses, internal kinetic as well as internal potential energy. Therefore, $E_q = E' + E$

Where E' = Potential energy , E = Kinetic energy

Average energy is given by

$$\frac{\int_{-\infty}^{\infty} \in F(v)\,dv}{\int_{-\infty}^{\infty} F(v)\,dv} = \frac{\int_{-\infty}^{\infty} \frac{1}{2}mv^2\left(\frac{m}{2\pi k_BT}\right)^{1/2} .Ne^{\frac{-E'-E}{2k_BT}} dv}{\int_{-\infty}^{\infty} N\left(\frac{m}{2\pi k_BT}\right)^{1/2} .e^{\frac{-E'-E}{2k_BT}} dv} = \frac{\frac{1}{2}m\int_{-\infty}^{\infty} v^2 e^{\frac{-\varepsilon}{2k_BT}} dv}{\int_{-\infty}^{\infty} e^{\frac{-\varepsilon}{2k_BT}} dv} = \frac{\frac{1}{2}m\,2\int_0^{\infty} v^2 e^{\frac{-mv^2}{2k_BT}} dv}{2\int_0^{\infty} e^{\frac{-mv^2}{2k_BT}} dv}$$

$$= \frac{\frac{1}{2}m\left(\frac{2k_BT}{m}\right)^{3/2}\int_0^{\infty} e^{-t} t^{3/2-1} dt}{\left(\frac{2k_BT}{m}\right)^{1/2}\int_0^{\infty} e^{-t} t^{1/2-1} dt} = \frac{1}{2}m\left(\frac{2k_BT}{m}\right)\frac{\frac{1}{2}\sqrt{\pi}}{\sqrt{\pi}} = \frac{1}{2}k_BT;\quad \bar{\varepsilon}_q = \frac{1}{2}k_BT$$

Thus according to Maxwell Boltzmann's statistics, the average kinetic energy per molecule associated with each degree of freedom is $\frac{1}{2}k_BT$. Which is the law of equipartition of energy.

Atomicity of gases: The internal energy U of this gas is the total kinetic energy of its molecules.

The internal energy

$$U = N \times \text{average K.E} = N \cdot \frac{n}{2}k_BT = \frac{n}{2}RT$$

Where n = degree of freedom.

$$C_V = \frac{dU}{dT} = \frac{d}{dT}\left(\frac{n}{2}k_BT\right) = \frac{n}{2}R;\ C_P - C_V = R;\ C_P = \left(\frac{n}{2}+1\right)R;$$

- **Ratio of specific heat**

$$\gamma = \frac{\left(\frac{n}{2}+1\right)R}{\frac{n}{2}R} = 1 + \frac{2}{n}$$

For monoatomic gas, $\gamma = 1 + \frac{2}{3} = \frac{5}{3} = 1.67$

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Diatomic gas, $\gamma = 1 + \frac{2}{5} = \frac{7}{5}$; Triatomic gas, $\gamma = 1 + \frac{2}{6} = \frac{4}{3}$

- **Root mean Square Speed**

  $v_{rms} = \sqrt{\frac{3RT}{M}}$

- **Mean Speed**

  $v_m = \sqrt{\frac{8RT}{\pi M}}$

  $k_B = R/N$ and M = Molar mass of the gas.

- Average translational energy per molecule $= \frac{3}{2k_BT}$

- Average kinetic energy of gas $= \frac{3}{2}nRT$

- **Vander Waals equation**

  $\left(\frac{P+a}{V^2}\right)(V-a) = nRT$

Mean free path is given by $\lambda = k_BT / \sqrt{2}\pi\sigma^2 P$ (where σ is the diameter of the molecule).

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Chapter 2

Laws of thermodynamics & their Consequences-1

Laws of thermodynamics :

(i) Zeroth law of thermodynamics :

If two system are separately in thermal equilibrium with a third system they are also in thermal equilibrium with each other.

This law enables us to compare the temperature of two system with the help of third system. This law can be used to define temperature.

The temperature of a system is the property which determines weather or not a system is in thermal equilibrium with other system.

First law of thermodynamics :

The first law of thermodynamics is simply the principle of conservation of energy applied to the system.

Whenever other forms of energy is converted into heat and viceversa there is a fixed ratio between quantities of energy & heat thus converted.

If an infinitesimal amount of heat dQ is given to the system then its some part is used to do work (dW) and other part is used to change the internal energy (dU)

$$dQ = dU + dW$$

Significance : This law signifies that

(i) Heat is a form of energy.

(ii) Energy is conserved in thermodynamic system.

(iii) Every thermodynamic system in equilibrium state possess internal energy which is a function of state only.

This law signifies the exact relation between heat & other energy. It follows directly from this law that it is impossible to derive any work without expenditure of an equal amount of energy in some other form.

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First law of Thermodynamics in different process :

(i) Cyclic Process :

$$dQ = dU + dW$$

For cyclic process $dU = 0$, because internal energy depends only on the state.

$$\int dQ = \int dW$$

ii) **Isochoric Process : (volume constant)**

$dQ = dU + dW$ but $dW = 0$, because $V =$ constant $dQ = dU$

If heat is given to the system internal energy increase & if heat is given by the system internal energy decrease.

iii) Adiabatic Process : (Q = constant)

$dQ = dU + dW$ or $Q =$ constant $\Rightarrow dQ = 0$

$dU + dW = 0$ or $dU = -dW = -PdV$

If work is done by the system (in adiabatic process) then internal energy decreases & vice-versa.

iv) Free expansion :

If a system say a gas expands in such a way that no heat enters or leave the system (adiabatic process) and also no work is done by or on the system then the process is called free expansion.

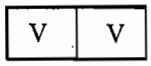
For free expansion $dQ = 0$ and $dW = 0$

$\Rightarrow dU = 0$ or $U = \text{constant}$

The initial and final state internal energy are same.

Q. 1. A perfectly insulated box contains a partition dividing the box into two equal parts as shown in the figure.

Initially L.H.S. part contain an ideal monoatomic gas at temperature T and other half is evacuated. The partition is suddenly removed so that the gas is filled through out the entire box.



(a) What is the final temperature of the gas

(b) What is the change in internal energy.

(c) What is the work done.

Soln. $dQ = dU + dW$

Since there is no transfer of heat $dQ = 0$

$P = 0, dW = 0, \Rightarrow dU = 0$

If internal energy is same, change in temperature is zero $T_1 = T_2$

Q. 2. Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = 0$

Where α and β are the coefficient of thermal expansion and coefficient of compressibility respectively.

Ans. Since V is a state function so we can write

$$\frac{\partial^2 V}{\partial T \partial P} = \frac{\partial^2 V}{\partial P \partial T} \text{ or } \frac{\partial}{\partial T}(-V\beta)_P = \frac{\partial}{\partial P}(V\alpha)_T \text{ as } \boxed{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\beta, \ \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha}$$

carrying out the differentiation we get

$$-\beta\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial \beta}{\partial T}\right)_P = \alpha\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial \alpha}{\partial P}\right)_T$$

or $$-\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial \alpha}{\partial P}\right)_T$$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$= -\frac{\beta}{V}(\alpha V) - \frac{\alpha}{V}(-\beta V) = 0$$

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Q. 3. Show that for homogeneous fluid $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$

where the symbols have their usual meaning.

(a) Hence prove that for a perfect gas

$$C_P - C_V = R$$

(b) Hence prove for a Vander Waal's gas

$$C_P - C_V = R\,(1 + 2a/RTV)$$

Ans. The secific heat at constant pressure and constant volume are given as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$[dQ = TdS]$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Now if the entropy S is regarded as a function of T and V and since dS is perfect differential
$S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

From Maxwell's I[st] relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Now $C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ (1)

(a) For a perfect gas the equation of state is $PV = RT$ (one mode)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right) = \frac{TR^2}{PV} = \frac{R^2T}{RT} = R$$

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(b) For a Vander Waal's gas the equation of state is

$$\left(P + a/V^2\right)(V - b) = RT \text{ (one mode)}$$

or $$\left(P + \frac{a}{v^2}\right) = \frac{RT}{V - b} \quad \ldots(2)$$

where a and b are constant

Differentiating eq[n] (2) w.r.t. T at constant volume we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Differentiating eq[n] (2) w.r.t. T at constant pressure we get

$$0-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P=-\frac{RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P+\frac{R}{V-b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{(V-b)^2}-\frac{2a}{v^3}\right]=\frac{R}{V-b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{v^3}\right]}$$

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in equation (1) we have

$$C_P-C_V=T\frac{R}{V-b}\cdot\frac{R}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]}=\frac{R^2T}{\frac{RT}{(V-b)^2}\left[1-\frac{2a}{V^3}\frac{(V-b)^2}{RT}\right]}$$

So $$C_P-C_V=\frac{R}{1-\frac{2a}{V^3}\frac{(V-b)^2}{RT}}$$

Neglecting b in comparision to V $(V \gg b) \Rightarrow V-b \approx V$

$$C_P-C_V=\frac{R}{1-\frac{2a}{V^3}\frac{V^2}{RT}}=\frac{R}{1-\frac{2a}{RTV}}=R\left(1-\frac{2a}{RTV}\right)^{-1}$$

Expanding binomially and neglecting higher powers we get

$$C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$$

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Q. 4. From the first law of thermodynamics deduce

(i) $dQ=C_V dT+\left[\left(\frac{\partial U}{\partial V}\right)_T+P\right]dV$ **(ii)** $C_P=C_V+\left[\left(\frac{\partial U}{\partial V}\right)_T+P\right]V\alpha$

(iii) $dQ=C_V dT+\frac{C_P-C_V}{V\beta}dV$

Ans. Consider a gaseous system whose thermodynamical state is described by any two of three variables (P, V & T)

Internal energy $U=f(T, V)$ ... (1)

According to Ist law of thermodynamics

$dQ = dU + dW$ ... (2)

where $dQ \rightarrow$ Amount of heat supplied to the system

$dU \rightarrow$ Change in the internal energy of the system

$dW \rightarrow$ Amount of work done by it.

If the change in the volume of the gas is dV then

$dW = PdV$ (at constant pressure) ... (3)

$\therefore \quad dQ = dU + PdV$ ... (4)

Since dU is a perfect differential

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad \text{... (5)}$$

Now equation (4) become

$$dQ = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \quad \text{... (6)}$$

when we are considering the changes in which there is a change in the temperature of the system, the changes at constant temperature would automatically reduce to zero.

Two distinct cases arise.

(i) $V = \text{constant} = dV = 0$

Then $dQ = \left(\frac{\partial U}{\partial T}\right)_V dT$

Heat capacity at constant volume

$$C_V = \left(\frac{dQ}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Hence eqn (6) becomes

$$\boxed{dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV} \quad \text{(6(a))}$$

(ii) Similarly $U = f(T,P)$ $V = f(T, P)$

$dQ = dU + PdV \Rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT \quad \text{... (7)}$$

If $U = f(V, P)$ as independent variables,

$$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV \quad \text{... (8)}$$

When $P = \text{constant} = dP = 0$

So equation (7) become

$$dQ = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

Hence heat capacity at constant pressure

$$C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

But $$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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So $$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$= \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

But co-eff of volume expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{So } \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

$$\therefore \quad C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\alpha \qquad \ldots (9)$$

(iii) From equation (9)

$$\left(\frac{\partial U}{\partial V}\right)_T + P = \frac{C_P - C_V}{V\alpha}$$

Substituting this value in equation (6(a)) we get

$$\boxed{dQ = C_V dT + \frac{C_P - C_V}{V\alpha} dV} \qquad \ldots (10)$$

Q. 5. For an ideal gas the molar heat capacity varies as $C = C_v + 3aT^2$. Find the equation of state for the process in the variables T and V where a is constant. C_v is heat capacity at constant volume.

Soln. $dQ = dU + dW$ $\qquad C dT = C_v dT + PdV \qquad (C_v + 3aT^2)dT = C_v dT + PdV$

$C_v dT + 3aT^2 dT = C_v dT + PdV \qquad 3aT^2 dT = PdV$

$$3aT^2 dT = \frac{nRT}{V} dV$$

$$3a\int T dT = nR\int \frac{dV}{V} \qquad 3a\frac{T^2}{2} = nR\ell n V/A \text{ [here A is a constant of integration]}$$

$$\frac{3a}{2}\frac{T^2}{nR} = \ell n\left(\frac{V}{A}\right), \qquad V = C e^{+3aT^2/2nR}$$

or $\boxed{V e^{-3aT^2/2nR} = \text{constant}}$

for an ideal gas $n = 1$

$\boxed{V e^{-3aT^2/2R} = \text{constant}}$

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Q. 6. Prove that the fall in temperature by the gas during the adiabatic expansion from pressure P_1 and P_2 at temperature T is given as

$$dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP = \frac{TV\alpha}{C_P} dP$$

Ans. The work done for the adiabatic expansion of a gas is

$W = PdV$ ... (i)

From Ist law of thermodynamics $\rightarrow dQ = dU + dW$

For adiabatic change $dQ = 0 \rightarrow dU = -dW = -PdV$

For I gm mole of the gas the change in internal energy for a change in temperature by dT is:

$$dU = C_V dT \quad \text{or} \quad dT = \frac{dU}{C_V} = -\frac{PdV}{C_V} \quad \text{... (ii)}$$

For perfect gas under adiabatic process

$$PV^\gamma = K(\text{constant})$$

$$PdV = -\frac{V^\gamma dP}{\gamma V^{\gamma-1}} = -\frac{V}{\gamma} dP$$

$$P\gamma V^{\gamma-1} dV + V^\gamma dP = 0 \quad \text{(iii)}$$

Now $PV = nRT$ for n mole of gas

$PdV + VdP = nRdT$

At constant pressure $dP = 0 \Rightarrow P\left(\frac{\partial V}{\partial T}\right)_P = nR$

Hence $PT\left(\frac{\partial V}{\partial T}\right)_P = nRT$

$\Rightarrow PT\left(\frac{\partial V}{\partial T}\right)_P = PV$ or $V = T\left(\frac{\partial V}{\partial T}\right)_P$

Substituting this value of V in equation (iii)

We get $PdV = -\frac{T}{\gamma}\left(\frac{\partial V}{\partial T}\right)_P dP$

From equation (ii) $dT = \frac{PdV}{C_V} = \frac{T}{C_V}\frac{1}{\gamma}\left(\frac{\partial V}{\partial T}\right)_P dP$ (using above equation)

Now $\gamma = \frac{C_P}{C_V}$

$$\therefore \quad \boxed{dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP} \quad \text{... (iv)}$$

The volume expansion of gas

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

Hence

$$\boxed{dT = \frac{TV\alpha}{C_P} dP = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP}$$

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Q. 7. If the degree of freedom of a gas is n, then find the ratio of C_p and C_v.

Soln. Molar specific heat $C_V = \frac{dU}{dT}$, $C_V = \frac{d}{dT}\left(\frac{n}{2}RT\right) = \frac{n}{2}R$

$$C_p - C_v = R, \qquad C_p = R + C_v = R + \frac{n}{2}R = \left(1+\frac{n}{2}\right)R$$

$$\therefore \frac{C_p}{C_v} = \frac{\left(\frac{n}{2}+1\right)R}{\frac{n}{2}R} \Rightarrow \boxed{\frac{C_p}{C_v} = 1+\frac{2}{n}}.$$

Q. 8. Gas equation during an adiabatic process : Prove $PV^\gamma = TV^{\gamma-1} = P^{\gamma-1}/T^\gamma$ = constant

Ans. Consider 1gm of ideal gas as working susbtance perfectly insulated from the sorrounding. Let the external work done by the gas be W. Applying first law of thermodynamics $dG = dU + dW$

But we know for adiabatic process $dQ = 0$ or $dQ = dU + dW$ and $dU = C_v dT$

So $0 = C_V dT + PdV = C_V dT + \frac{PdV}{J}$ $(dW = PdV)$

As the external work is done by the gas at the cost of its internal energy, so there is a fall in temperature by dT

$dU = 1 \times C_V \times dT$

$$C_V\, dT + \frac{PdV}{J} = 0 \quad \text{(i)}$$

$dQ = dU + dW$

$= CdT + PdV + VdP$

for constant P $\Rightarrow (dQ)_P = C_P dT + PdV$

for constant U $\Rightarrow (dQ)_V = C_V dT + VdP$

Adiabatic $\Rightarrow dQ = 0 = (dQ)_P + (dQ)_V$

$\Rightarrow C_P dT = -PdV$ ...(i)

and $C_V dT = -VdP$ ...(ii)

Dividing (i) by (ii)

$$\Rightarrow \frac{C_P}{C_V} = \frac{P}{dP}\frac{dV}{V}$$

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Integrating $\gamma \log V + \log P = \text{const}$ $\log PV^\gamma = \text{constant}$

Again $PV = RT$ $\Rightarrow$ $P = \frac{RT}{V}$

$\left(\frac{RT}{V}\right)V^\gamma = \text{const}$ or $R\,TV^{\gamma-1} = \text{constant}$

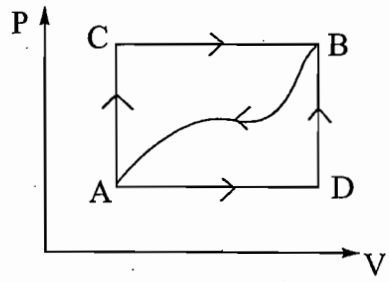
$$\Rightarrow \gamma\frac{dP}{P} = \frac{dV}{V}\left(\because \frac{C_P}{C_V} = \gamma\right) \text{integrating} \Rightarrow \boxed{PV^\gamma = \text{constant}}$$

Q. 9. When a system is taken from the state A to the state B along the path ACB, 80 joule of heat flows into the system and the system does 30 joule of work.

(i) How much heat flows into the system along the path ADB if work done is 10 J ?

(ii) The system is returned from state B to state A along the curved path. The work done on the system is 20 joule. Does the system absorb or liberate heat and how much?

(iii) If $U_A = 0$, $U_D = 40$ J. Find the heat absorbed in the process AD & DB.



(i) $W = 10J$

Heat along ADB

Ans. $dQ = dU + dW$

$= 50 + 10 = 60$ Joule

$\left\{\begin{array}{l}\because dQ = dU + dw \\ \Rightarrow dU = 80 - 30 = 50 \text{ Joule}\end{array}\right.$

(ii) $dW = -20J$

$dQ = dU + dW$

$= 50 - 20 = 30$ Joule

Liberated heat $= 80 - 30 = 50$ Joule

(iii) $U_A = 0 \quad U_D = 40J$

for path DB $= \delta W = 0 \Rightarrow dQ = dU$

$(U_B - U_A) = 80J \qquad = 80J$

for path AD $dU = U_D - U_A = 40J$

$dQ = dU + dW$

$= 40 + 10 = 50$ joule $\left\{\begin{array}{l}\text{for DB } dW = 0 \\ \text{for ADB } dW = 10J\end{array}\right.$

Q. 10. A motor car tyre has a pressure of 2 atomsphere at room temperature 27°C. If the tyre suddenly bursts. Find the resulting temperature.

Ans. $P_1 = 2$ atomsphere $\qquad P_2 = 1$ atomsphere

$T_1 = 27°C = 27 + 273 = 300$ K $\qquad T_2 = ?$

$\gamma = 1.4$ for air

Formula $\dfrac{P_1^{\gamma-1}}{T_1^{\gamma}} = \dfrac{P_2^{\gamma-1}}{T_2^{\gamma}}$

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\frac{1}{2}\right)^{1.4-1} = \left(\frac{T_2}{30\upsilon}\right)^{1.4}$$

$$\left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

Taking log both side

$0.4 \log 0.5 = 1.4 \log T_2 - 1.4 \log 300$

$= \quad -0.1204 = 1.4 \log T_2 - 3.4680$

$1.4 \log T_2 = 3.4680 - 0.1204 = 3.3476$

$\log T_2 = 3.3476/1.4 = 2.3911$

$T_2 = 246.1$ K $= -26.9°C$

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Q. 11. A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the i) pressure and ii) temperature.

Ans. Given $P_1 = 1$ atm $\qquad P_2 = ? \qquad \gamma = 1.4$

$V_1 = V \qquad V_2 = V/2 \qquad T_1 = 27°C = 300K \qquad T_2 = ?$

$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 1\left(\frac{V}{\frac{V}{2}}\right) = 1(2)^{1.4} = 2.636 \text{ atm}$$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300\left(\frac{V}{\frac{V}{2}}\right)^{1.4-1}$$

$$= 300(2)^{0.4} = 395.9\text{K} = 122.9^\circ\text{C}$$

Q. 12. Air is compressed adiabatically of half its volume. Calculate the change in its temerature.

Let the initial temperature be T_1K and final temperature T_2K

Initial volume $V_1 = V$ and final volume $V_2 = \frac{V}{2}$

For adiabatic process $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{ or } T_2 = T_1(2)^{1.4-1}$$

$$T_2 = [2]^{0.4}T_1 = 1.319T_1$$

So change in temperture.

$$T_2 - T_1 = 1.319T_1 - T_1 = 0.319T_1\text{K}$$

Q. 13. 1 gm molecule of a monoatomic $\left(\gamma = \frac{5}{3}\right)$ perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmosphere. Calculate the resulting difference in temperature.

Ans. Given $P_1 = 1$ atm $P_2 = 50$ atm $T_1 = 27^\circ\text{C} = 300\text{K}$

$T_2 = ?$ $\gamma = 5/3$

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2} \text{ or } \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$(50)^{\frac{5}{3}-1} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}} \Rightarrow 50^{\frac{2}{3}} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}}$$

$$\frac{2}{3}\log 50 = \frac{5}{3}\log T_2 - \frac{5}{3}\log 30$$

$$T_2 = 1434\text{ K} = 1161^\circ\text{C}$$

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WORK DONE DURING AN ISOTHERMAL PROCESS

Q. 14. A certain gas obeys the eqn of state $P(V-b) = RT$

(i) Derive an expression for heat and work in a reversible isothermal expansion of the gas

(ii) Derive an expression for heat and work in a reversible adiabatic expansion of the gas

(iii) Calculate ΔU, Q and W when 1 mol of the gas expands reversibly at 300K from 0.220 to 20.02 litre

(i) isothermally (ii) adiabatically. Assume that b = 0.020 lit mol^{-1}, $C_V = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$

Ans. (i) $dW = -PdV$ or $W = \int_{V_1}^{V_2} PdV$

Given Eq. of state is $P = \dfrac{RT}{(V-b)}$

Thus $W = -\int_{V_1}^{V_2} \dfrac{RT}{V-b}dV = -RT\ell n\left(\dfrac{V_2-b}{V_1-b}\right)$

Now, $dU = \left(\dfrac{\partial U}{\partial V}\right)dV + \left(\dfrac{\partial U}{\partial T}\right)dT$ $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P = T\left[\dfrac{\partial\left(\dfrac{RT}{V-b}\right)}{\partial T}\right]_V - P$

$= \dfrac{RT}{V-b} - P = P - P = 0$

$\because \Delta U = 0$

Thus $Q = \Delta U - W = -W$

$= +RT\,\ell\left(\dfrac{V_2-b}{V_1-b}\right)$

(ii) for adiabatic reversible expansion $\rightarrow Q = 0$

Hence $dU = dW$ $\begin{cases} dU = C_V dT \\ dW = PdV \end{cases}$

$= -\dfrac{RT}{V-b}dV$

$\Rightarrow \int_{T_1}^{T_2}\dfrac{C_V dT}{T} = -\int_{V_1}^{V_2}\dfrac{R}{V-b}dV \Rightarrow C_V\ell n\left(\dfrac{T_2}{T_1}\right) = -R\ell n\left(\dfrac{V_2-b}{V_1-b}\right)$

$\Rightarrow \dfrac{T_2}{T_1} = \left(\dfrac{V_2-b}{V_1-b}\right)^{-R/C_V} = \left(\dfrac{V_2-b}{V_1-b}\right)^{-(\gamma-1)}$

$\therefore w = \Delta U = C_V(T_2 - T_1)$

$= C_V T_1\left[\left(\dfrac{V_1-b}{V_2-b}\right)^{\gamma-1} - 1\right]$

(iii) $T_1 = T_2 = 3ooK$ $V_1 = 0.220$ litre $V_2 = 20.020$ litre, $b = 0.020$ litre

For isothermal reversible expansion

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$$W = -Q = -RT_1 \ \ell n\left(\frac{V_2 - b}{V_1 - b}\right)$$

$$= -(8.314)(300)\,\ell n\left(\frac{20.0}{0.20}\right)$$

$$= -11.548 \text{ KJ mol}^{-1}$$

$$\Delta U = 0$$

Now, for an adiabatic reversible expansion

$Q = 0$ thus

$$\Delta U = W = C_V T_1\left[\left(\frac{V_1 - b}{V_2 - b}\right)^{\gamma - 1} - 1\right]$$

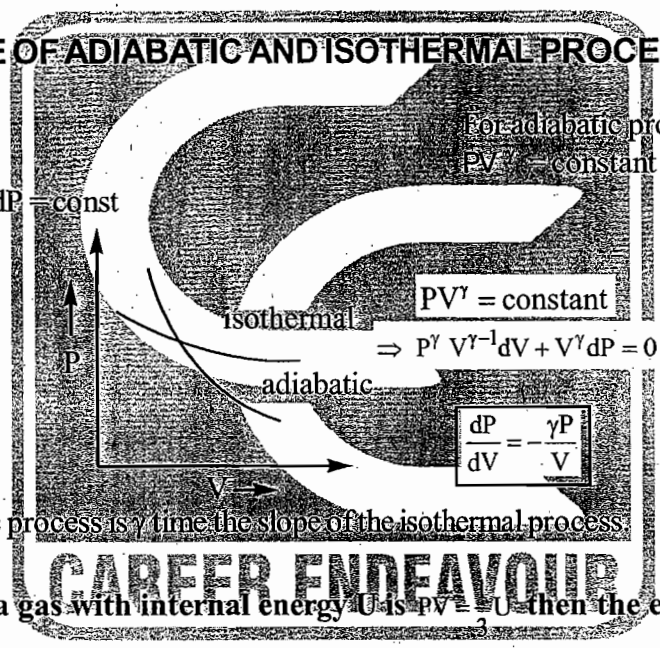
Given $C_V = \frac{3}{2}R$, $\gamma = \frac{5}{3}$ and $T_1 = 300$ K

$$\Delta U = W = \left(\frac{3}{2}R\right)(300)\left[\left(\frac{200}{20000}\right)^{2/3} - 1\right] = -3.554 \text{ kJ.}$$

SLOPE OF ADIABATIC AND ISOTHERMAL PROCESS

For isothermal processes
$PV = \text{constant}$
Differenciating $PdV + VdP = \text{const}$

$$\Rightarrow \frac{dP}{dV} = -\frac{P}{V}$$



The slope of an adiabatic process is γ time the slope of the isothermal process.

Q. 15. If the eqn of state for a gas with internal energy U is $PV = \frac{1}{3}U$ then the equation for an adiabatic process is:

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(i) $PV^{1/3} = \text{const}$ **(ii)** $PV^{2/3} = \text{const}$ **(iii)** $PV^{4/3} = \text{const}$ **(iv)** $PV^{3/5} = \text{const}$

Ans. For adiabatic process $dQ = 0$

$$dU = -dW = -PdV$$

But $PV = \frac{1}{3}U \rightarrow U = 3PV$

$$d(3PV) = -PdV = 3\,PdV + 3\,VdP = -PdV$$

$$3\,VdP = -4PdV \text{ or } \frac{dP}{P} = -\frac{4}{3}\frac{dV}{V}.$$

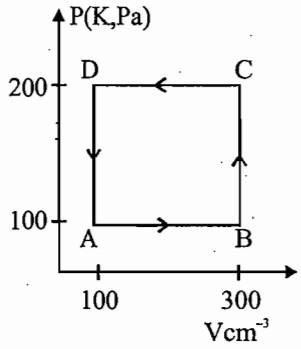
Integrating $\log P = -\frac{4}{3}\log V + \log C$

$\log P + \log V^{4/3} = \log C \Rightarrow \log PV^{4/3} = \log C$ here C is a constant

$$\boxed{PV^{\frac{4}{3}} = \text{constant}}$$

(iii) option is correct

Q. 16. A thermodynamic system is taken through the cycle ABCDA as shown in figure. (i) Calculate the work done by the gas (system) during the path AB, BC, CD, DA. (ii) Find the total heat rejected by the gas during the process ABCDA.



Ans. (i) $W_1 = PdV = 100\ KPa \times 200\ cm^{-3}$ (along AB)

$$= 100 \times 1000 \times \frac{200}{10^6}\ \frac{Pa}{m^3} = 20\ J$$

$W_2 = 0$ because the change in volume = 0 (along BC)

$W_3 = -P \times dV = 200\ KP_a \times 200\ cm^{-3}$

$$= -200 \times 1000 \times \frac{200\ Pa}{10^6\ m^3}$$

$= -40\ J$ (along CD)

The –ve sign is due to decrease in volume

$W_4 = 0$ (along DA)

$\therefore \quad W = W_1 + W_2 + W_3 + W_4 = 20 - 40 = -20\ J$

(ii) $dQ = dU + dW$

For cyclic process $dU = 0$

$dQ = dW = -20J \rightarrow$ Heat rejected by the gas

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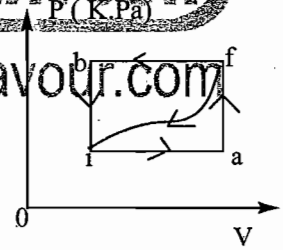
Q. 17. When a system is taken from a state i to f along the path i a f as shown in figure. It is found that heat Q absorbed by the system is 50 cal and the work done by the system is 20 cal Along the path i b f Q = 36 cal



(i) What is the work done alone the path i bf ?

(ii) If the work done on the system is equal to 13 cal for the curved returned path fi. What is the value Q for this path ?

(iii) If U of the system in initial state is equal to 10 cal. What is the internal energy of the system in final state ?

(iv) If internal energy of the system for state B = 22 cal. What are the values Q for the process b f and i b?

Ans. Given $U_i = 10$ cal $\quad Q = 50$ cal and $W = 20$ cal

for the path i a f

(i) $\quad Q = U_f - U_i + W$

$\Rightarrow \quad 50 = U_f - 10 + 20$

$\Rightarrow$ $\boxed{U_f = 40 \text{ cal}}$

So work done along ibf

as $dQ = 36$

$dQ = dU + dW$

$\Rightarrow$ $dW = dQ - dU = 36 - (40-10) = \boxed{6 \text{ cal}}$

(ii) $W = 13$ cal for (of $\rightarrow$ i), $W = -13$ cal, $dQ = dU + dW$

$= (U_i - U_f) - 13 = -30 - 13 = -43$ Cal

(iii) $\Delta U = 30$

$\Rightarrow U_f - U_i = 30 \quad \Rightarrow U_f - 10 = 30 \Rightarrow \boxed{U_f = 40}$

(iv) $U_b = 22$ cal $\quad U_i = 10$ cal

So for path b f $\Rightarrow U_f - U_i = 18$ cal

$\Rightarrow$ for b $\rightarrow$ $\Delta W = 0$

so $dQ = dU$

$\Rightarrow$ $\boxed{dQ = 18 \text{ cal}}$

For path i $\rightarrow$ b

$\Delta U = U_b - U_i = 12$

$dQ = \Delta U + dW$

As $\Delta w = 6$ {because for b $\rightarrow$ f $\Delta W = 0$

$dQ = 12 + 6 = 18$ cal

$\Rightarrow$ $\boxed{dQ = 18 \text{ cal}}$

Q. 18. An ideal gas expands adiabatically but quasistatically from state i($P_i V_i T_i$) to a state f($P_f V_f T_f$). What is the change in its internal energy? What would this change be if the expansion were isothermal?

Ans. Quasistatic process : If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium, the process is called quasistastic this means we can specify pressure, volume, temperature uniquely at any instant during such a process. Thus a quasistastic process is an idealised process in which all changes take place infinitely slowly from 1st law $dQ = dU + dW$

But for adiabatic process $dQ = 0$

So $dU = -dW$

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Total change in internal energy $= \int_i^f dU = -\int_i^f PdV = -\int_i^f \frac{K}{V^\gamma} dV$

So $U_f - U_i = -K\left(\frac{V^{-\gamma+1}}{-\gamma+1}\right)_i^f$ $\quad \begin{cases} \text{as } PV^\gamma = K \\ P = \frac{K}{V^\gamma} \end{cases}$

$= \frac{K}{1-\gamma}\left(V^{-\gamma+1}\right)_i^f$

But $P_i V_i^\gamma = P_f V_f^\gamma = K$

So $U_f - U_i = \frac{1}{1-\gamma}\left(P_f V_f^\gamma \, V_f^{-\gamma+1} - P_i V_i^\gamma \, V_i^{-\gamma+1}\right)$

$= \frac{1}{1-\gamma}(P_f V_f - P_i V_i)$ $\quad$ use $PV = RT$

$$\boxed{\Delta U = \frac{R}{1-\gamma}(T_f - T_i)}$$

(ii) for isothermal expansion $T_i = T_f$

$$U_f - U_i = \frac{R}{1-\gamma}(T-T) = 0$$

So for quasistatic isothermal process, the change in internal energy is Zero.

Q. 19. Figure shows a process ABCA performed on an ideal gas. Find the net heat given to the system during the process.

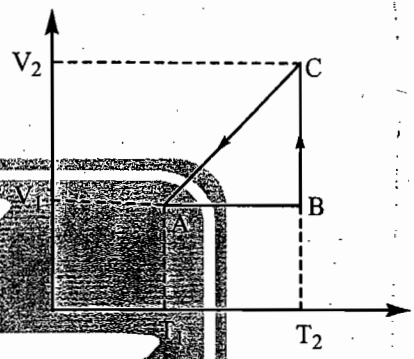
Ans. Since the process is cyclic so the change in internal energy $dU = 0$

Since $dU = 0 \Rightarrow dQ = dW = PdV$

For the process AB change in volume = Zero

$\Rightarrow W_1 = 0$

For process BC $\rightarrow$ Temp is constant



$$W_2 = \int_{V_1}^{V_2} dW_2 = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{TR}{V} dV$$

$$W_2 = RT\ell n\, V\Big]_{V_1}^{V_2} = RT_2 \ell n \frac{V_2}{V_1}$$

For process $AC \rightarrow \frac{V}{T} = \text{constant}$

$$PV = RT \Rightarrow \frac{V}{T} = \frac{R}{P} \Rightarrow V = \frac{RT}{P} \rightarrow dV = \frac{R}{P} dT$$

$$W_3 = \int_{T_2}^{T_1} dW = \int_{T_2}^{T_1} PdV = \int_{T_2}^{T_1} P\frac{R}{P} dT = [RT]_{T_2}^{T_1} = R(T_1 - T_2)$$

$$W_3 = R(T_1 - T_2)$$

Now $Q = W = W_1 + W_2 + W_3 = R\left[T_2 \ell n \frac{V_2}{V_1} + (T_1 - T_2)\right]$

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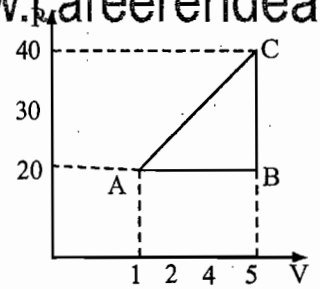
Q. 20. A gas is carried through a cycle ABCA as shown in the P-V diagram fig. Determine whether the heat is given to the system or by the system. Work done by the system or on the system. Internal energy of the system increases or decreases in the following process.



(i) For the process AB if $\Delta U = +Ve$

(ii) For the process BC if $Q = +Ve$

(iii) For process CA

(iv) For AB net work done in the complete cycle.

Ans. (i) $\Delta U = +Ve$ (given) $\rightarrow$ so internal energy of the system increase

$\Delta W = +Ve$ (work done by the system because volume increase)

$\Delta Q = \Delta U + \Delta W = +Ve$ (Heat given to the system)

(ii) For BC

$Q = +Ve$ (given) $\rightarrow$ Heat given to the system

$\Delta W = 0$ (because V = Const $W = PV$, $dV = 0$, So $W = 0$)

$\Delta U = +Ve$ $\Delta Q = \Delta U + \Delta W$. Internal energy of the system increase)

(iii) For process CA

For process ABC $\Delta U = +Ve$ $\left(\because (\Delta U)_{AC} = (\Delta U)_{AB} + (\Delta U)_{BC} = +Ve + +Ve\right.$

For CA Process $(\Delta U)_{CA} = -(\Delta U)AC = -Ve$

$(\Delta U)_{CA} = -ve$ (Internal energy of the system decrease)

$\Delta W = -ve$ ($\because$ volume decrease so workdone on the system)

$\Delta Q = -ve$ ($\Delta Q = \Delta U + \Delta W = -ve$, heat is given by the system)

(iv) Net workdone in couple cycle = area under the curve

$$= \frac{1}{2} \times AB \times BC = 1/2 \times 3 \times 20 = 30 \text{ Joule.}$$

Q. 21. Fig shows the process A and B on a system. Let ΔQ_1 and ΔQ_2 be the heat given to the system in the process A and B respectively. Then,

(i) $\Delta Q_1 > \Delta Q_2$ **(ii)** $\Delta Q_1 = \Delta Q_2$ **(iii)** ΔW **(iv)** $\Delta Q_1 \leq \Delta Q_2$

Ans. Since ΔU is same for both the process and ΔW is the amount of work which is represented by the area under the curve.

$\Delta Q = \Delta U + \Delta W \rightarrow \Delta Q$ will vary as ΔW

Since area under A is greater than area under B

$\Rightarrow \Delta W_A > W_B$, so $\Delta Q_1 > \Delta Q_2$

If both the arrow signs are changed then

$\Delta Q_1 < \Delta Q_2$

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Q. 22. P, V and T for a certain gas are related by $P = \frac{\alpha T - \beta T^2}{V}$, where α and β are constants. Find the workdone by the gas if the temperature changes from T_1 to T_2 while pressure remains constant.

Soln. $PV = RT$, $PdV = RdT$, ($\because$ Pressure is constant)

$$dV = \frac{RdT}{P},$$

$dW = PdV = \alpha T - \beta T^2$ $dW = \alpha dT - 2\beta T dT$,

$$W = \alpha \int_{T_1}^{T_2} (\alpha dT - 2\beta T dT) \qquad W = \alpha(T_2 - T_1) - \beta(T_2^2 - T_1^2).$$

REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process : A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the opposite order and sense and no changes are left in any of the bodies taking part in the process or in the sorrounding.

The condition for reversibility :

A process can be reversible only when it satisfy two condition.

(i) Process must be quasistatic (If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium)

A quasistatic process is an idealised process in which all changes take place infinitely slowly.

(ii) Process must be non-dissipiative (dissipiative force such as friction, resistance, Hysteresis etc must be completely absent).

Q. 23. Classify the reversible & irreversible process among the following:

Ans. (1) Isothermal expansion of a gas → irreversible

(2) Isothermal quasistatic expansion of a gas → Reversible

(3) Adiabatic expansion of a gas → Irreversible

(4) Diffusion of a gas → irreversible

(5) Transfer of heat from hot body to cold body → irreversible

(6) Free expansion of a perfect gas → irreversible

(7) Transfer of heat by radiation → irreversible

(8) Electrical heating of wire → irreversible

(9) Very slow expansion or contraction of a spring → Reversible.

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Problems that appeared in GATE from this section :

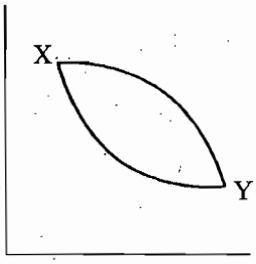
G-1. A piston containing an ideal gas is originally in the state X (see figure). The gas is taken through a thermal cycle X→Y→X as shown. The work done by the gas is positive if the direction of the thermal cycle is:

(a) clockwise

(b) counter - clockwise

(c) neither clockwise nor counter-clockwise

(d) clockwise from X→Y and counter-clockwise from Y→X.



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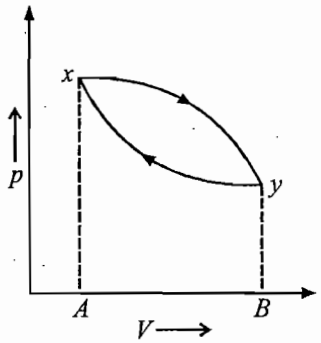
[GATE-2003]

Soln. Since, work done = Area between p-V curve and volume axis



Hence, work in positive direction is clockwise.

$\therefore$ W_{xy} = Area $xyBA$ and W_{yx} = Area $yBAx$ and $W_{xy} > W_{xy} = W_{yx}$

Hence correct option is (a).

G-2. **The equation of state of a dilute gas at very high temperature is described by $\frac{PV}{k_BT} \approx 1 + \frac{B(T)}{V}$, where V is the volume per particle and $B(T)$ is a negative quantity. One can conclude that this is a property of**

(a) a Vander Waal's gas **(b) an ideal Fermi gas**
(c) an ideal Bose gas **(d) an ideal inert gas**

[GATE-2004]

Soln. The gas equation for real gas can be written as $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ ...(i)

where, a and b are known as Vander Waal's coefficients and equation is known as Vander Waal's gas equation.

By rearranging the above equation, we have

$$\Rightarrow \quad P = \frac{-a}{V^2} + \frac{RT}{V - b}$$

Multiplying by volume V on both sides in the above equation,

$$PV = \frac{-a}{V} + \frac{RT}{V - b} \cong \frac{-a}{V} + RT \qquad (\because V \gg b)$$

$$= k_BT - \frac{a}{V} \qquad [R = Nk_B \text{ and for one mole gas we have } R = k_B]$$

$$\text{or} \quad \frac{PV}{k_BT} = 1 - \frac{a}{k_BTV}$$

$$\Rightarrow \frac{PV}{k_BT} \simeq 1 + \frac{B(T)}{V} \qquad \left[\text{where, } \frac{a}{k_BT} = B(T)\right]$$

Hence correct option is (a).

G-3. **The isothermal compressibility, κ of an ideal gas at temperature T_0 and volume V_0, is given by**

(a) $-\frac{1}{V_0}\frac{\partial V}{\partial P}\Big|_{T_0}$ **(b)** $\frac{1}{V_0}\frac{\partial V}{\partial P}\Big|_{T_0}$ **(c)** $V_0\frac{\partial P}{\partial V}\Big|_{T_0}$ **(d)** $V_0\frac{\partial P}{\partial P}\Big|_{T_0}$

[GATE-2012]

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Soln. Bulk modulus or isothermal incompressibility of an ideal $= -\frac{\partial p}{\partial V/V_0}\Big|_{T_0}$

Hence, compressibility $= -\frac{1}{V_0}\frac{\partial V}{\partial p}\Big|_{T_0}$

Hence correct option is (a).

G-4. **For a gas under isothermal conditions, its pressure P varies with volume V as $P \propto V^{-5/3}$. The bulk modulus B is proportional to**

(a) $V^{-1/2}$ **(b)** $V^{-2/3}$ **(c)** $V^{-3/5}$ **(d)** $V^{-5/3}$

[GATE-2014]

Soln. According to ideal gas equation, we get $PV = nk_BT$. For isothermal condition, we get $dPV + PdV = 0$.

$$\Rightarrow \quad P = -\frac{dP}{dV/V} = B$$

So, $P = B$ ...(i)

But given that $P \propto V^{-5/3}$ ...(ii)

Comparing equations (i) and (ii), we get $B \propto V^{-5/3}$.

Hence correct option is (d).

G-5. Two gases separated by a impermeable but movable partition are allowed to freely exchange energy. At equilibrium, the two sides will have the same

(a) pressure and temperature **(b) volume and temperature**

(c) pressure and volume **(d) volume and energy**

[GATE-2013]

Soln. Once the system is released freely, due to exchange of energy both sides will attain thermal equilibrium by attaining the same temperature. Also, due to unbalanced pressure, both the sides will attain mechanical equilibrium by balancing the pressure on both sides of the movable wall.

Hence correct option is (a).

G-6. If the isothermal compressibility of a solid is $\kappa_T = 10^{-10}\,(Pa)^{-1}$, the pressure required to increase its density by 1% is approximately.

(a) $10^4\ Pa$ **(b)** $10^6\ Pa$ **(c)** $10^8\ Pa$ **(d)** $10^{10}\ Pa$

[GATE-2011]

Soln. $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = 10^{-10}(Pa)^{-1} = -\frac{1}{V}\frac{dV}{dP}$

$$\rho = \frac{m}{V} \Rightarrow d\rho = -m\frac{1}{V^2}\cdot dV$$

$$\frac{d\rho}{\rho} = \frac{-\frac{m}{V^2}dV}{\frac{m}{V}} = -\frac{1}{V}dV = dP\,\kappa_T$$

$$\Rightarrow dP = \frac{1}{\kappa_T}\left(\frac{d\rho}{\rho}\right) = \frac{0.01}{\kappa_T} = \frac{0.01}{10^{-10}} = 10^8\,Pa$$

Hence correct option is (c).

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G-7. A sample of ideal gas with initial pressure P and volume V is taken through an isothermal expansion proceed during which the change in entropy is found to be ΔS. The universal gas constant is R. Then the work done by the gas is given by

(a) $(PV\Delta S)/(nR)$ **(b)** $nR\Delta S$ **(c)** PV **(d)** $(P\Delta S)/(nRV)$

[GATE-2003]

Soln. By ideal gas equation, $PV = nRT$ ...(i)

and $\Delta S = \frac{\Delta Q}{T}$ ...(ii)

Multiplying equations (i) and (ii),

$$PV\Delta S = nR\Delta Q$$

$$\Rightarrow \Delta Q = \frac{PV\Delta S}{nR}$$

$\because$ For isothermal expansion $\Delta U = 0$

$$\Rightarrow W = \Delta Q = \frac{PV\Delta S}{nR}$$

Hence correct option is (a).

G-8. The mean free path of the particles of a gas at temperature T_0 and pressure p_0 has a value λ_0. If the pressure is increased to 1.5 p_0 and the temperature is reduced to 0.75 T_0, the mean free path

(a) remains unchanged. **(b) is reduced to half**

(c) is doubled **(d) is equal to 1.125 λ_0**

[GATE-2002]

Soln. The mean free path of the particle of a gas at a temperature T_0 may be given as $\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$ where, σ is the diameter of the molecule and n be the number of molecules per unit volume. For pressure P_0 and temperature T_0, then mean free path λ_0 may be given as $\lambda_0 = \frac{1}{\sqrt{2}\pi\sigma^2 n}$ where, $n = \frac{P}{k_B T}$

So, $\lambda_0 = \frac{k_B T_0}{\sqrt{2}\pi\sigma^2 P_0}$, For $P_1 = 1.5P_0$, $T_1 = 0.75T_0$, we have

$$\lambda_1 = \frac{k_B T_1}{\sqrt{2}\pi\sigma^2 P_1} = \frac{k_B \times 0.75T_0}{\sqrt{2}\pi\sigma^2 \times 1.5P_0} = \frac{0.5}{\sqrt{2}\pi\sigma^2}\frac{k_B T_0}{P_0} = \frac{\lambda_0}{2}$$

Hence correct option is (b).

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G-9. The internal energy of n moles of a gas is given by $E = \frac{f}{2}nRT - \frac{an}{V}$ where V is the volume of the gas at temperature T and a is a + ve constant one mole of the gas in state (T_1, V_1) is allowed to expand adiabatically into vacuum to a final state (T_2, V_2). The temperature T_2 is:

(i) $T_1 + \frac{a}{R}\left(\frac{1}{V_2} + \frac{1}{V_1}\right)$ **(ii)** $T_1 - \frac{2}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

(iii) $T_1 + \frac{2}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$ **(iv)** $T_1 - \frac{1}{3}\frac{a}{R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$

[GATE-2006]

Ans. Since the process is free expansion process. So the change in internal energy for free expansion process is Zero

$$\bar{E}_2 - \bar{E}_1 = 0$$

$$\frac{3}{2}nRT_1 - \frac{a}{V_1} = \frac{3}{2}nRT_2 - \frac{a}{V_2}$$

$$\frac{3}{2}nRT_2 = \frac{3}{2}nRT_1 - \frac{a}{V_1} + \frac{a}{V_2}$$

$$= \frac{3}{2}nRT_1 + a\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

For $n = 1$

$$\boxed{T_2 = T_1 + \frac{2a}{3R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}$$

Hence correct option is (c).

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Chapter 3

Laws of thermodynamics & their Consequences-2

Second law of thermodynamics:

The 1st law of thermodynamics tells that energy of the universe remain constant. This law tell us that heat and mechanical work both are interconvertible. It doesn't tell us the limitation and condition for this conversion i.e how much heat is converted into work and weather the transformation itself can take place or not (The direction of transformation). Thus 1st law simply tells that if a process take place, energy will remain conserve. It doesn't tell us weather the process is possible or not. The condition of transformation of heat into work (whether the process is possible or not) is specified by the 2nd law of thermodynamics. There are two equivalent statements of 2nd law of thermodynamics.

Kelvin – Plank Statement : It is impossible for a self acting device or machine unadded by any external agency to convert heat from a cold body to a hot body or heat can't flow spontaneously from a cold body to a hot body. Kelvin Plank and Clausis statement are equivalent. Any process which violates Kelvin Plank statement also violate Clausius statement. Any process which violate Kelvin-Plank and Clausius statement would also violate the principle of increase in entropy

$(\Delta S)_{universe} \geq 0$

$\rightarrow \Delta S = 0$ for Reversible process

$\Delta S > 0$ for irreversible or natural process

$dS = \frac{dQ}{T}$ Mathematical form of 2nd law of thermodynamics

For reversible process $\Delta S = \oint \frac{dQ}{T} = 0$

The entropy of an isolated system can never decrease - entropy of a system measures the disorder of the system

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CARNOT THEOREM

I^st Statement : All the reversible engine working between source and sink have the same efficiency whatever the working substance

$$e_{R_1} = e_{R_2}$$

2nd statement : irreversible engine working between source and sink can never be more efficient then a reversible engine working between same source and sink

$$e_{R_1} = e_{R_2} > e_I$$

entropy of an isolated system can never decrease.

Complete conversion of work into heat is possible but the reverse is not possible.

Heat engine:

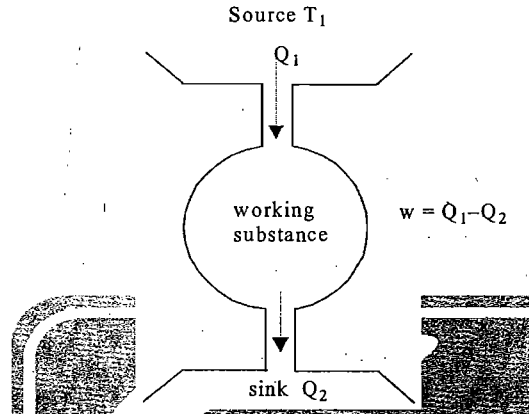
A cyclic device that converts heat taken from the source into mechanical work is called a heat engine.

The net amount of work done by the substance $W=Q_1-Q_2$

Efficiency : Efficiency of a heat engine is defined as the ratio of the work obtained to heat taken in form the source in one cycle.

$$\eta=\frac{W}{Q_1}=\frac{Q_1-Q_2}{Q_1}=1-\frac{Q_2}{Q_1}$$

$\eta=1$ when $Q_2=0$ i.e the sink is at absolute Zero which is impossible.



Indicator diagram :

The resultant PV diagram of a system undergoing a process is called indicator diagram. This diagram enables us to represent the working of an engine and to calculate useful work from the system (engine)

Reversible engine :

The engine based on reversible cycle is called reversible engine (Carnot reversible engine).

(i) A cylinder with perfectly heat insulating walls but perfectly conducting base and closed with a tight fitting perfectly insulating and frictionless piston, filled with fixed mass of perfect gas as a working substance.

(ii) A hot body of infinitely large heat capacity at constant temperature T_1 (source)

(iii) A cold body of infinitely large heat capacity at constant temperature T_2 (sink)

(iv) A perfectly heat insulating stand.

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Q_1 = heat taken from the source during Process AB

Q_2 = heat given to the sink from the system during process CD

Catnot's Cycle

$$W_{AB}=Q_1=\mu RT_1\log\frac{V_2}{V_1}$$

$$W_{CD}=Q_2=\mu RT_2\log\frac{V_3}{V_4}$$

$$W_{BC}=\frac{\mu R}{\gamma-1}(T_2-T_1)$$

$$W_{DA}=\frac{\mu R}{\gamma-1}(T_2-T_1)$$

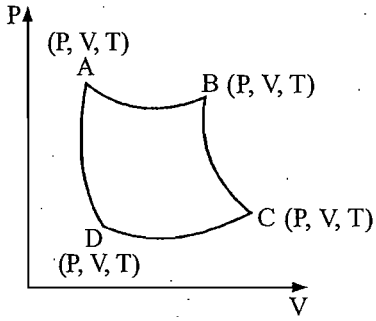

Fig. Carnot Cycle

AB → isothermal expansion

BC → adiabatic expansion

CD → isothermal compression

DA → adiabatic compression

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \mu RT_1 \log \frac{V_2}{V_1} + \mu RT_2 \log \frac{V_3}{V_4}$$

Efficiency :

$$\eta = \frac{W}{Q} = 1 - \frac{Q_2}{Q_1} \qquad \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \log \frac{\frac{V_3}{V_4}}{\frac{V_2}{V_1}}$$

Since the curve BC and DA represents adiabatiac expansion and compression respectively.

$$TV^{\gamma-1} = \text{Const}$$

So $$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \qquad \text{... (i)}$$

and $$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \qquad \text{... (ii)}$$

Dividing (i)/(ii)

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\Rightarrow \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

So $$\eta = 1 - \frac{Q_2}{Q_1} \quad \text{or} \quad \eta = 1 - \frac{T_2}{T_1}$$

Refrigerator :

A device that remove heat from a cold body and adding it to a hot body with the help of external agency. It is the reverse of heat engine.

Co-efficient of performance of a refrigirator :

It is the ratio heat taken in from the cold body to work done by external device need to run the refrigirator

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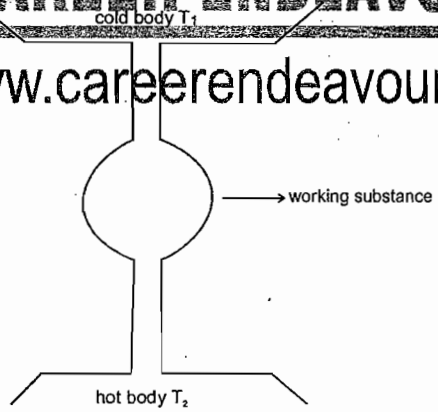

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

But we know $$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

So $$K = \frac{1}{\frac{T_1}{T_2} - 1} = \frac{T_2}{T_1 - T_2}$$

So $$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

Relation between efficiency of a carnot engine (η) and co-efficient of performance (K) :

$$\eta = \frac{T_1 - T_2}{T_1} \qquad \text{and} \qquad K = \frac{T_2}{T_1 - T_2}$$

$$\text{Now} \quad K + 1 = \frac{T_1}{T_1 - T_2} \Rightarrow \frac{1}{K+1} = \frac{T_1 - T_2}{T_1} = \eta$$

$$\boxed{\eta = \frac{1}{K+1}}$$

A good refrigirator should have a high co-efficient of performance.

ENTROPY

One of the most common interpretation of entropy is done by saying that the entropy is the measure of disorderness of the system. It means more the orderness is present in the system less will be its entropy. Similarly, more the disorderness present in the system more will be its entropy. For example : The entropy of boiling water is more than the entropy of ice. Also, one of the common means for knowing the change in entropy of the system (for spontaneous-irreversible processes), is that the change in entropy will always be positive i.e., for irreversible spontaneous process the *entropy of the universe* always increases.

Mathematically the change in entropy for a reversible process is defined as :

$$dS = \frac{đQ_R}{T}$$

$$\Rightarrow \int_{S_i}^{S_f} dS = \int_i^f \frac{đQ}{T} \qquad \Rightarrow \qquad \boxed{\Delta S = S_f - S_i = \int_i^f \frac{đQ}{T}}$$

In the above definition S is an exact differential. It means that, just like internal energy the entropy is also state function. For the case of irreversible process, the change in entropy is calculated by replacing the irreversible process with a reversible process between the same initial and final states.

In order to understand the physical meaning of entropy and its significance, it is necessary to study *all* the entropy changes that take place when a system undergoes a reversible process. If we calculate the entropy change of the system and add the calculated entropy change of the surroundings, then we obtain the sum of the entropy changes brought about by this particular process. We may call this sum the *entropy change of the universe* due to the process in question.

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The following table shows the calculation of change in entropy for various irreversible processes.

Type of irreversibility	Irreversible process	Entropy change of the system	Entropy change of the local surroundings	Entropy change of the universe
External mechanical irreversibility	Isothermal dissipation of work through a system into internal energy of a reservoir	0	$\frac{W}{T}$	$\frac{W}{T}$
	Adiabatic dissipation of work into internal energy of a system	$C_P \ell n \frac{T_f}{T_i}$	0	$C_P \ell n \frac{T_f}{T_i}$
Internal mechanical irreversibility	Free expansion of an ideal gas	$nR \ell n \frac{V_f}{V_i}$	0	$nR \ell n \frac{V_f}{V_i}$
External thermal irreversibility	Transfer of heat through a medium from a hotter to a cooler reservoir	0	$\frac{Q}{T_2} - \frac{Q}{T_1}$	$\frac{Q}{T_2} - \frac{Q}{T_1}$
Chemical irreversibility	Diffusion of two dissimilar inert ideal gases	$2nR \ell n \frac{V_f}{V_i}$	0	$2nR \ell n \frac{V_f}{V_i}$

Isoentropic process : A reversible process during which the entropy of a system remains constant is called isoentropy process.

According to 2nd law of thermodynamics $dQ = TdS$

For adiabatic process $dQ = 0 \Rightarrow dS = 0 \Rightarrow S = \text{constant}$

A reversible adiabatic process is an isoentropic process for irreversible process $dS > 0$.

Q. 24. From the law of thermodynamics prove the following relation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$ **and hence show that the internal energy of an ideal gas is independent of its volume but not so for an actual gas.**

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Soln. I st law of thermodynamics $dQ = dU + PdV$

2nd law of thermodynamics $dQ = T\,d\,S$

Combining these two laws $TdS = dU + PdV$

$$\Rightarrow \quad dS = \frac{1}{T} dU + \frac{P}{T} dV$$

Hence we can write at constant temperature

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \quad \Rightarrow \quad T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P$$

Using Maxwell's thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ the above equation become

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P$$

so $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ ... (i)

Now (i) $PV = RT \Rightarrow P = \frac{RT}{V}$

$\frac{\partial P}{\partial T} = \frac{R}{V}$

Put this value in eqn (i)

$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V} - P$ $\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \left(\because \frac{RT}{V} = P\right)$

Hence internal energy of an ideal gas is independent of volume

(ii) $\left(P + a/V^2\right)(V - b) = RT$ $P = \frac{RT}{V-b} - \frac{a}{V^2}$ $\frac{\partial P}{\partial T} = \frac{R}{V-b}$

Put this value in eqn (i)

$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V-b} - P$

$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

Hence internal energy of an real gas depends on volume. (All the above treatment is done for 1 mode of gas).

Q. 25. The mass M of a liquid at temperature T_1 is mixed with an equal mass of same liquid at temperature T_2. The system is thermally insulated. Show that the entropy change of the universe is

is called

$2MC_P \log_e \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$.

Ans. When M gm of the liquid at temperature T_1 is mixed with an equal mass of same liquid at temp T_2 the temperature of the mixture will be $\frac{T_1 + T_2}{2}$

Now change in entropy when the temp of one gm of liquid changes from T_1 to $\frac{T_1+T_2}{2}$

$\Delta S_1 = \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{dQ}{T} = \int_{T_1}^{\frac{T_1+T_2}{2}} MC_P\, dT/T = MC_P \log_e \frac{T_1+T_2}{2T_1}$

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Also the change in entropy when the temp of M gm of liquid changes from T_2 to $\frac{T_1 + T_2}{2}$

$$\Delta S_2 = \int_{T_2}^{\frac{T_1+T_2}{2}} MC_P\, dT/T = MC_P \log_e \frac{T_1+T_2}{2T_2}$$

Hence the entropy change of the universe

$\Delta S = \Delta S_1 + \Delta S_2$

$$= MC_P \log_e \frac{T_1+T_2}{2T_1} + MC_P \log_e \frac{T_1+T_2}{2T_2}$$

$$= MC_P \log_e \left[\frac{T_1+T_2}{2T_1} \times \frac{T_1+T_2}{2T_2}\right]$$

$$= MC_P \log_e \left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right)^2$$

$$\Delta S = 2MC_P \log_e \frac{T_1+T_2}{2\sqrt{T_1T_2}}$$

which is necessarily + Ve.

Q. 26. For an isobaric process prove the relation

(i) $\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S$ (ii) $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$

Ans. In the set of four thermodynamic variable (P, V, T, S) only two are independent variables while other two may be expressed as their functions.

We can represent pressure P as the function of two independent variables S and T i.e.

$$P = P(S,T) \quad dP = \left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{\partial T}\right)_S dT$$

For an isobaric process $dP = 0$

Hence

$$\left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{dT}\right)_S dT = 0$$

$$\left(\frac{\partial P}{\partial S}\right)_T dS = -\left(\frac{\partial P}{\partial T}\right)_S dT$$

$$\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S$$

(ii) Again we represent the pressure as the function of T and V

$$P = P(T, V)$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

For an isobaric process $dP = 0$

$$\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T dV = -\left(\frac{\partial P}{\partial T}\right)_V dT$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

Q. 27. Prove the thermodynamic relation

(i) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ **(ii)** $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

Ans. Let the entropy S of a thermodynamic system be a function of temperature T and volume V i.e.

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$S \equiv f(T, V)$

Since dS is a perfect differential so we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \ldots (i)$$

Since $TdS = dQ$

For any substance the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

From Maxwell's first relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Making these substitution in eqn (i)

$$\boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \rightarrow \text{Required relation}$$

(ii) Let the entropy S of a thermodynamic system be function of temperature T and pressure P i.e

$S = f(T, P)$

Since dS is a perfect differential

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad \ldots (ii)$$

For any substance the specific heat at constant pressure is given by $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

From Maxwell's II[nd] realtion $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

making these substitution in equation (ii)

$$\boxed{TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$$

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Q. 28. Find the efficiency of the carnot engine working between the steam point and the ice point.

Ans. Given $T_1 = 100°C = 100 + 273 = 373$ K $\quad T_2 = 0°C = 0 + 273 = 273$ K

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{373 - 273}{373} = \frac{100}{373}$$

$$\% \text{ of efficiency} = \frac{100}{373} \times 100 = 26.81\%.$$

Q. 29. A carnot engine whose temperature of the source is 400 K takes 300 calories of heat at this temperature and reject 150 calories of heat to the sink. What is temperature of the sink. Also calculate the efficiency of the engine?

Ans. $H_1 = 200\,Cal \qquad H_2 = 150\,Cal \quad T_1 = 400\,K \qquad T_2 = ?$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2} \Rightarrow T_2 = \frac{H_2}{H_1} \times T_1 = \frac{150}{200} \times 400 = 300^{\circ}K$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

% of efficiency $0.25 \times 100 = 25\%$.

Q. 30. A carnot engine is operated between two reservoirs at temperature of 450° and 350° K. If the engine receives 1000 calories of heat from the source in each cycle. Calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine & the work done by the engine in each cycle (1 calorie = 4.2J)

Ans. $T_1 = 450^{\circ}K$ $T_2 = 350^{\circ}K$ $H_1 = 1000$ cal $H_2 = ?$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1} \Rightarrow H_2 = \frac{T_2}{T_1} \times H_1 = \frac{350}{450} \times 1000 = 777.77\,cal$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350}{450} = \frac{100}{450} = 0.2222$$

% of efficiency = 22.22%

work done in each cycle $= H_1 - H_2$

$= 1000 - 777.77\,Cal = 222.23$

$= 222.23 \times 4.2\,5 = 933.335$ joule.

Q. 31. A carnot engine working as a refrigerator between 260 K and 300 K receives 500 calories of heat from the reservoir at the lower temperature calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of workdone in each cycle to operate the refrigerator.

Ans. $Q_1 = ? \qquad Q_2 = 500\,cal \qquad T_1 = 260K \qquad T_2 = 300K$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow Q_1 = \frac{Q_2}{T_2} \times T_1 = \frac{500 \times 260}{300} = 576.92\,cal$$

$W = Q_1 - Q_2 = 76.92$ cal $= 76.42 \times 42 = 323.08$ joule.

Q. 32. A carnot's refrigerator takes heat from water at 0°C and discard it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the co-efficient of performance of the machine?

Ans. $Q_1 = ? \qquad Q_2 = 1000 \times 80 = 80{,}000$ cal. $\qquad L = 80$ Cal/g (Latent heat of ice)

$T_1 = 300K \qquad T_2 = 273^{\circ}K$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_1 = \frac{T_1}{T_2} \times Q_2 = \frac{80000 \times 300}{273} = 87{,}900\,cal.$$

work done by the refrigirator

$$W = J(Q_1 - Q_2) = 4.2(87900 - 80000)$$

$$= 4.2 \times 7900 = 3.183 \times 10^4\,J$$

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$$\text{co-efficient of performance} = \frac{Q_2}{Q_1 - Q_2} = \frac{80,000}{87900 - 80,000}$$

$$= \frac{80,000}{7900} = 10.13$$

Q. 33. A carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased.

$$\eta = 50\% = 0.5 \quad T_2 = 273 + 7 = 280\ K \quad T_1 = ?$$

$$\eta = 1 - \frac{T_2}{T_1} = 0.5 = 1 - \frac{280}{T_1}$$

$$\frac{280}{T_1} = 0.5 \quad \Rightarrow \quad T_1 = \frac{280}{0.5} = \frac{2800}{5} = 560\ K$$

In the 2nd case

$$\eta^1 = 70\% = 0.7$$

$$T_2 = 280K \qquad T_1 = ?$$

$$\eta = 1 - \frac{T_2}{T_1}$$

$$0.7 = 1 - \frac{280}{T_1} \Rightarrow \frac{280}{T_1} = 0.3 \Rightarrow T_1 = \frac{280}{0.3} = 933.33\ K$$

So increase in temperature $= 933.33 - 560 = 372.33\ K$

Q. 34. Calculate the expression for efficiency of carnot engine in terms of adiabatic expanssion ratio (ρ)

Ans. $\left(\frac{V_3}{V_2}\right) = \rho$ is called adiabatic expansion ratio (as above)

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{1}{\rho}\right)^{\gamma-1}$$

$$\therefore \quad \boxed{\eta = 1 - \frac{T_2}{T_1} = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} = 1 - \frac{Q_2}{Q_1}}$$

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Q. 35. Two identical bodies of constant heat capacities at temperature T_1 and T_2 $(T_1 > T_2)$ are used as reservoirs for a heat engine. Assuming that the bodies don't undergo any phase change and remain at constant pressure P. Show that the amount of work obtained is given by

$$W = C_P (T_1 + T_2 - 2T_f)$$

Where T_f is the final temperature of the bodies. Also show that W is maximum when $T_f = \sqrt{T_1 T_2}$

Ans. The working substance takes heat from the body at temperature T_1 and after doing work gives the balance heat to the body at temperature T_2. This process continues untill T_1 drops to T_f and T_2 rises to T_f

The total heat taken from the hot body

$$Q_1 = C_P (T_1 - T_f) \qquad \ldots (i)$$

heat given to the cold body

$$Q_2 = C_P (T_f - T_2) \qquad \ldots (ii)$$

The balance $(Q_1 - Q_2)$ converts into work

$$W = Q_1 - Q_2 = C_P(T_1 - T_f) - C_P(T_f - T_2), \quad W = C_P(T_1 - T_f - T_f + T_2) = C_P(T_1 + T_2 - 2T_f)$$

The heat Q_1 is taken in at a mean temperature $= \frac{T_1 + T_f}{2}$

heat Q_2 is given out at a mean temperature $= \frac{T_2 + T_f}{2}$

Carnot engine have max efficiency so the work done must be maximum

$$\frac{Q_1}{Q_2} = \frac{\frac{T_1 + T_f}{2}}{\frac{T_2 + T_f}{2}} = \frac{T_1 + T_f}{T_2 + T_f}$$

From equation (i) and (ii)

$$\frac{Q_1}{Q_2} = \frac{T_1 - T_f}{T_f - T_2}$$

So $\frac{T_1 + T_f}{T_2 + T_f} = \frac{T_1 - T_f}{T_f - T_2}$

$\Rightarrow \quad T_f = \sqrt{T_1 T_2}$

Q. 36. In a carnot cycle isothermal expansion of an ideal gas take place at 400°K & the isothermal compression at 300°K during the expansion 500 cal of heat energy are transfered to the gas. Determine
(1) The work performed by the gas during isothermal expansion.
(2) The heat rejected from the gas during an isothermal compression
(3) The work done in isothermal compression of gas

Ans. (1) The work performed by the gas during the isothermal expansion is equivalent to heat Q_1 absorbed by the gas

Here $Q_1 = 500$ cal

$W = 500 \times 4.18 = W/J = Q$

$= 2090$ Joule

(2) Let Q_2 be the amount of heat rejected

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = \frac{300}{400} \times 500 = 375 K$$

(3) The work done on the gas during isothermal compression is equivalent to the heat rejected

$W = Q_2 = 375$ cal $= 375 \times 4.18 = 1567.5$ joule

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Q. 37. A reversible engine workes between two temperature whose difference is 100°C. If 746 J of heat from the source is taken and 546 J heat is given to the sink by working substance calculate the temperature of the source and sink?

Ans. Given $T_1 - T_2 = 100 \qquad Q_1 = 746, \qquad Q_2 = 546$

use $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{Q_1}{Q_2} = \frac{746}{546} = \frac{373}{273}$

$$\frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \Rightarrow \frac{200}{546} = \frac{100}{T_2} \Rightarrow T_2 = \frac{546 \times 100}{200} = 273$$

Now $T_1 - T_2 = 100 \quad \rightarrow \quad T_1 = T_2 + 100 = 273 + 100 = 373.$

Q. 38. An ideal carnot heat engine takes 100 cal of heat at 627°C from a source and rejects a part at 27°C to the sink. Find the work done by the engine per cycle, the heat rejected to the sink per cycle & the efficiency of the engine.

Ans. $Q_1 = 100$ cal $\quad T_1 = 627°C$

$Q_2 = ?$ $\quad T_2 = 27°C$

Let the temperature of the sink = x

Now $\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{100}{x} = \frac{627}{27} \rightarrow x = \frac{1000 \times 27}{627} = 333.3$ cal

So the heat reject per cycle to the sink = 333.3 cal

Now $W = Q_1 - Q_2 = 1000 - 333.3 = 666.7$ cal $= (666.7 \times 4.12)$ joule

Now, $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{27}{627} = \frac{600}{627} = \frac{200}{209}$

Q. 39. The efficiency of a carnot cycle is $1/6$, on reducing the temperature of the sink by 65°C the efficiency increases to $1/3$. Find the initial and final temperature between which the cycle it is working

Ans. $1 - \frac{T_2}{T_1} = 1/6 \Rightarrow \frac{T_1 - T_2}{T_1} = \frac{1}{6} \Rightarrow 6T_1 - 6T_2 = T_1$

or $5T_1 - 6T_2 = 0$ ...(i)

$1 - \frac{(T_2 - 65)}{T_1} = \frac{1}{3} \Rightarrow \frac{T_1 - T_2 + 65}{T_1} = \frac{1}{3} \Rightarrow 3T_1 - 3T_2 + 195 = T_1$

$2T_1 - 3T_2 = -195$ ...(ii)

Solving eqn (i) and (ii)

$5T_1 - 6T_2 = 0$

$2T_1 - 3T_2 = -195$

Solving $T_1 = 390$ K

$5T_1 = 6T_2 \Rightarrow 5 \times 390 = 6T_2 \Rightarrow T_2 = \frac{5 \times 390}{6} = 325$ K

Q. 40. For a carnot engine using an ideal gas the adiabatic expansion ratio is 5 and value of $\gamma = 1.4$, calculate the efficiency of the engine.

Ans. $\eta = 1 - \left(\frac{1}{P}\right)^{\gamma - 1} = 1 - \left(\frac{1}{5}\right)^{1.4-1} = 1 - \left(\frac{1}{5}\right)^{0.4} = 0.48$

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Q. 41. Two carnot engines are operating in series. The 1st engine absorbs a quantity of heat Q_1 at a temperature T_1 and after doing work W_1 rejects the remaining heat Q_2 at lower temperature T_2. The second engine absorbs the heat Q_2 at temperature T_2 (rejected by 1st) and after doing work W_2 rejects the remaining heat Q_3 at a still lower temperature T_3. Compute the efficiency of the combination.

Ans. $W = (Q_1 - Q_2) + (Q_2 - Q_3) = Q_1 - Q_3$

η (efficiency) $= \frac{W}{Q_1} = \frac{Q_1 - Q_3}{Q_1} = 1 - \frac{Q_3}{Q_1}$

But $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ and $\frac{Q_1}{Q_3} = \frac{T_1}{T_3}$

So $\eta = 1 - \frac{T_3}{T_1}$.

Problems that appeared in GATE from this section :

G-1. **The pressure versus temperature diagram of a given system at certain low temperature range is found to be parallel to the temperature axis in the liquid to solid transition region. The change in the specific volume remains constant in this region. The conclusion one can get from the above is**
(a) the entropy of solid is zero in this temperature region
(b) the entropy increases when the system goes from liquid to solid phase in this temperature region
(c) the entropy decreases when the system transforms from liquid to solid phase in this region
(d) the change in entropy is zero in the liquid to solid transition region

[GATE-2008]

Soln. P-T curve is parallel to the temperature axis

$\Rightarrow$ slope of the curve = 0

$$\Rightarrow \frac{dP}{dT} = 0 \qquad ...(i)$$

Now, from Clausius-Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V} \qquad ...(ii)$$

We know $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

$\therefore$ from (i) $\Delta S = 0$.

Hence, the correct option is (d).

G-2. **For any process, the second law of thermodynamics requires that the change of entropy of the universe be**
(a) positive only **(b) positive or zero** **(c) zero only** **(d) negative or zero**

[GATE-2004]

Soln. $\Delta S = 0$; for a perfectly reversible (ideal) process.

$\Delta S > 0$; otherwise (all irreversible process).

$\therefore \Delta S \geq 0$.

Hence correct option is (b).

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G-3. **Consider a system of N atoms of an ideal gas of type A at temperature T and volume V. It is kept in diffusive contact with another system of N atoms of another ideal gas of type B at the same temperature T and volume V. Once the combined system reaches equilibrium,**
(a) the total entropy of the final system is the same as the sum of the entropy of the individual system always.
(b) the entropy of mixing is $2Nk_B \ell n 2$.
(c) the entropy of the final system is less than that of sum of the initial entropies of the two gases.
(d) the entropy of mixing is non-zero when the atoms A and B are of the same type.

[GATE-2008]

Soln. Entropy of mixing is always non-zero and positive for a classical ideal gases. In case both gases are of same type, volume T and having same number of molecules ; the entropy of mixing = $2N k_B \ell n 2$.
Hence correct option is (d).

G-4. **The entropy function of system is given by S(E) = a E (E_0 – E) where a and E_0 are positive constants. The temperature of the system is**

(c) decreases monotonically with energy (d) zero

[GATE-2013]

Soln. $\frac{1}{T}=\frac{dS}{dE} \Rightarrow \frac{1}{T}=a E_0-2aE \Rightarrow T=\frac{1}{(a E_0-2aE)}$.

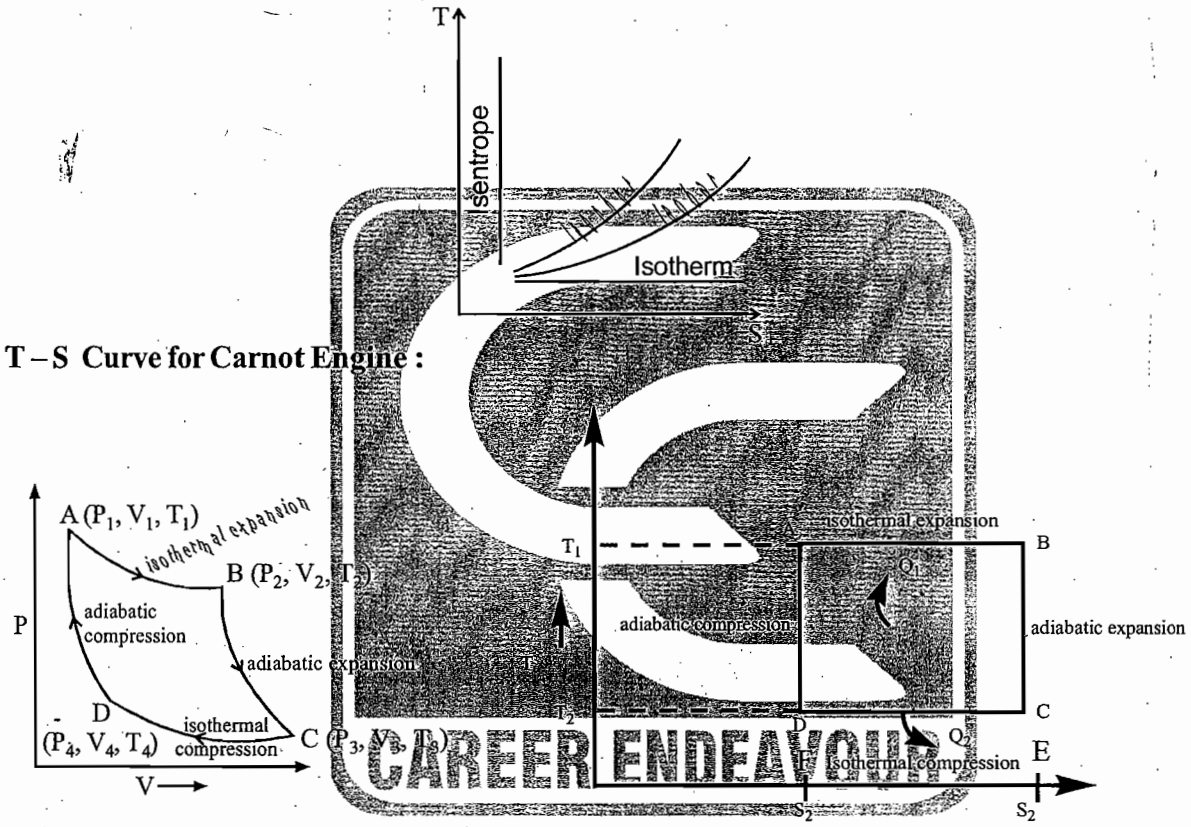
This means that T is continuous and will be positive for $E < E_0$ and negative for $E > E_0$.

Hence correct option is (a).

S-T Diagram:

Just like the PV-diagram is important for studying thermodynamics of an ideal gas, TS-diagram is important for studying the entropy changes taking place in various processes. The following figures schematically show the entropy changes taking place in various processes with the help of TS-curves.

T – S Curve for Carnot Engine :



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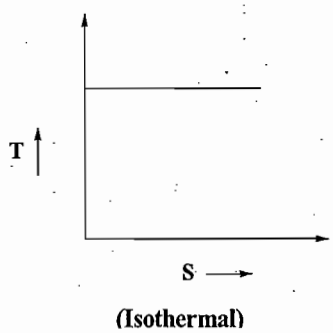
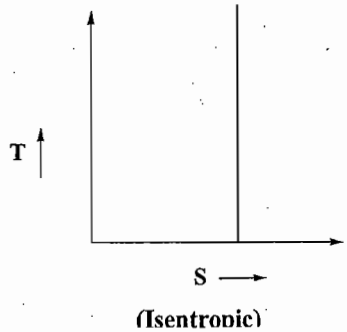
Area under PV curve represents amount of work done. Area of the cycle on T – S curve represent heat transfer.

$$\eta=\frac{W}{Q}=\frac{\text{Area of ABCD}}{\text{Area of ABEF}}$$

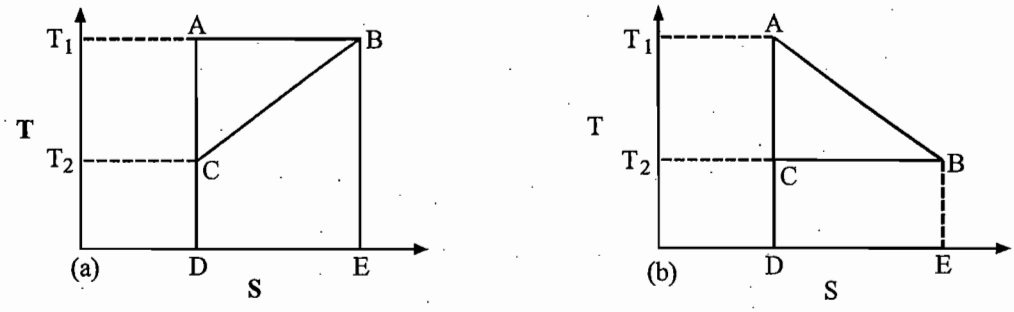


(Isothermal)



(Isentropic)

Q. 42. Compare the efficiency of the following cycles : →



Ans. If Q_1 be the amount of heat absorbed during the process in which entropy increases and Q_2 be the amount of heat rejected during the process in which entropy decreases

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Area of ABC}}{\text{Area of ABED}}$$

Area of ABC for fig (a) = Area of ABC for fig (b)

Area of ABED for fig (A) < Area of ABED for fig (b)

$$\Rightarrow \eta_a < \eta_b$$

In a T–S diagram the slope of an isochoric process $\rightarrow \frac{T}{C_V}$

In a T–S diagram the slope of an isobaric process $\rightarrow \frac{T}{C_P}$

$$\frac{\text{Slope of isochoric}}{\text{Slope of isobaric}} = \frac{T/C_V}{T/C_P} = \frac{C_P}{C_V} = \gamma$$

Q. 43. Calculate the change in entropy when an ideal gas undergoes reversible isothermal expansion from initial volume V_i to final volume V_f.

Ans. $dQ = TdS \Rightarrow dS = \frac{dQ}{T}$

$$\Delta S = S_f - S_i = \int_{Vi}^{Vf} \frac{dQ}{T}$$

According to first law of thermodynamics $dQ = dU + dW$

$dU = 0$ because the process is reversible–isothermal expansion

$$dQ = dW = PdV$$

So $$\Delta S = \int_{Vi}^{Vf} \frac{PdV}{T}$$

But we know $PV = \mu RT \Rightarrow \frac{P}{T} = \frac{\mu R}{V}$

$$\Delta S = \int_{Vi}^{Vf} \frac{\mu R}{V} dV = \mu R \left[\ell n\, V\right]_{Vi}^{Vf} = \mu R \ell n \frac{V_f}{V_i}$$

Q. 44. Calculate the change in entropy when a liquid is heated from T_1 to T_2 $(T_2 > T_1)$.

Ans. Let a liquid of mass m specific heat C is heated from T_1 to T_2

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If dQ is the amount of heat taken by the liquid to rise its temperature by dT then

$$dQ = mCdT \qquad (\because\ Q = mc\Delta T)$$

Corresponding change in entropy

$$dS = \frac{dQ}{T} = \frac{mCdT}{T}$$

Entropy change in the entire process

$$(\Delta S)\ \text{liquid} = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} mC\frac{dT}{T} = mC\left[\ell n\, T\right]_{T_1}^{T_2}$$

$$(\Delta S)\ \text{liquid} = mC\ \ell n\frac{T_2}{T_1}$$

nount of

Which is +ve($\because T_2 > T_1$). Thus entropy of liquid increases.

Change in entropy on cooling :

$$\Delta S = mC\ \ell n\frac{T_2}{T_1}$$

Here $T_2 < T_1$ (cooling). So the entropy of the liquid decreases

Q. 45. Calculate the change in entropy when ice (a) melts to water (b) changes into steam :

Ans. (a) when ice changes to water at 0°C the change in entropy

$$\Delta S = \int\frac{dQ}{T} = \frac{Q}{T} = \frac{ML}{T}$$

where M = mass of liquid, L = latent heat

(i) The change in entropy when ice is converted in water at 0°C

$$\Delta S_1 = \frac{ML}{T_1} \qquad L = 80\ \text{Kcal/gm}$$

n from

The change in entropy when water is at 0°C and at 100°C

$$\Delta S_2 = mc\ \ell n\frac{T_2}{T_1}$$

The change in entropy when water at 100°C converted into steam

$$\Delta S_3 = \frac{mL}{T_2} = 540\ \text{Kcal/gm}$$

So total change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= \frac{mL}{T_1} + mc\ \ell n\frac{T_2}{T_1} + \frac{ml}{T_2}$$

Q. 46. A body of mass m_1, specific heat c_1 and temperature T_1K is thermally connected with another body of mass m_2, specific heat c_2 and at temperature T_2. Derive an expression for change in entropy.

Ans. Let $T_1 > T_2$ and T be the equilibrium temperature

According to the principle of calorimetry

$$m_1c_1(T_1 - T) = m_2c_2(T - T_2)$$

$$m_1c_1T_1 - m_1c_1T = m_2c_2T - m_2c_2T_2$$

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$$m_1c_1T + m_2c_2T = m_1c_1T_1 + m_2c_2T_2$$

$$T = \frac{m_1c_1T_1 + m_2T_2c_2}{m_1c_1 + m_2c_2}$$

The change in entropy when the body comes from T_1 to T

$$\Delta S_1 = m_1c_1 \int_{T_1}^{T} \frac{dT}{T} = m_1c_1 \ell n \frac{T}{T_1} \qquad (T_1 > T)$$

The change in entropy when the body come from T_2 to T ($T_2 < T$)

$$\Delta S_2 = m_2c_2 \int_{T_2}^{T} \frac{dT}{T} = m_2c_2 \ell n \frac{T}{T_2}$$

Total change in entropy $\Delta S = \Delta S_1 + \Delta S_2$

$$\Delta S = m_1c_1 \ell n \frac{T}{T_1} + m_2 c_2 \ell n \frac{T}{T_2}$$

$$= \ell n \left(\frac{T}{T_1}\right)^{m_1c_1} + \ell n \left(\frac{T}{T_2}\right)^{m_2c_2}$$

$$\Delta S = \ell n \left[\left(\frac{T}{T_1}\right)^{m_1c_1} \left(\frac{T}{T_2}\right)^{m_2c_2}\right] > 0$$

Q. 47. Derive an expression for the change in entropy of a perfect gas in terms of its pressure volume and specific heat undergoing on one mole of change in state.

Ans. Let us consider one mole of perfect gas at pressure P, volume V and temperature T. When an infinitesimal amount of heat dQ is added to it the increase in entropy is

$$dS = \frac{dQ}{T}$$

From 1st law $dQ = dU + dW$

But $dU = C_V dT$ and $dW = PdV = RT\frac{dV}{V}$

so $dQ = C_V dT + RT\frac{dV}{V}$

$$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + R\frac{dV}{V}$$

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The total change in entropy

$$S = \int \frac{dQ}{T} = C_V \int \frac{dT}{T} + R \int \frac{dV}{V} \qquad \ldots (i)$$

From ideal gas eqn. $PV = RT$

$$dT = \frac{PdV + VdP}{R}$$

and $R = C_P - C_V$

$$\therefore S = C_V \int \frac{PdV + VdP}{RT} + R \int \frac{dV}{V}$$

$$= C_V \int \frac{PdV + VdP}{PV} + (C_P - C_V) \int \frac{dV}{V}$$

$$= C_V \int \frac{dV}{V} + C_V \int \frac{dP}{P} + C_P \int \frac{dV}{V} - C_V \int \frac{dV}{V}$$

$$= C_V \int \frac{dP}{P} + C_P \int \frac{dV}{V}$$

$$\boxed{S = C_V \log P + C_P \log V + \text{constant}}$$

If a gas passes from an initial state P_i, V_i, T_i to P_f, V_f, T_f then the change in entropy of the gas is

$$\boxed{\Delta S = C_V \log \frac{P_f}{P_i} + C_P \log \frac{V_f}{V_i}}$$

Q. 48. Derive an expression for change in entropy of a perfect gas in terms of its temperature, pressure and specific heat at constant pressure.

Ans. $dQ = dU + dW = C_V dT + PdV = C_V dT + RT\frac{dV}{V} = TdS$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

$$\Delta S = \int_i^f dS = \int_i^f \frac{C_V dT}{T} + R\int_i^f \frac{dV}{V} = C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f}{V_i}$$

ume and

Again $\frac{PV}{T} = \text{const} \Rightarrow \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \Rightarrow \frac{V_f}{V_i} = \frac{P_i T_f}{P_f T_i}$

nitesima

$$\Delta S = C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f}{V_i} = C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{P_i}{P_f} + R \ell n \frac{T_f}{T_i}$$

$$= C_V \ell n \frac{T_f}{T_i} - R \ell n \frac{P_f}{P_i} + R \ell n \frac{T_f}{T_i}$$

$$= (C_P - R) \ell n \frac{T_f}{T_i} - R \ell n \frac{P_f}{P_i} + R \ell n \frac{T_f}{T_i}$$

$$= C_P \ell n \frac{T_f}{T_i} - R \ell n \frac{P_f}{P_i}$$

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Q. 49. Calculate the change in entropy of a Vander Waal's gas as its state changes from $V_i T_i$ to $V_f T_f$. Equation of state for one mole of Vanderwaal's gas is

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$\left(P + \frac{a}{V^2}\right)(V - b) = RT$ **where a, b – Vander Waal's constant**

Ans. $dS = \frac{dQ}{T}$: (2^{nd} law of thermodynamics)

$dQ = dU + dW$: (1^{st} law of thermodynamics)

$dU = C_V dT \qquad dW = \left(P + \frac{a}{V^2}\right)dV = \frac{RT}{V-b}dV$

$$dS = \frac{dU + dW}{T} = \frac{C_V dT + \frac{RT}{(V-b)}dV}{T}$$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V-b}$$

The change in entropy when the gas passes from the state V_i, T_i to V_f, T_f is:

$$\Delta S = S_f - S_i = \int_i^f dS = C_V \int_i^f \frac{dT}{T} + R\int_i^f \frac{dV}{V-b}$$

$$= C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f - b}{V_i - b}$$

$$\boxed{\Delta S = C_V \ell n \frac{T_f}{T_i} + R \ell n \frac{V_f - b}{V_i - b}}$$

Problems that appeared in GATE from this section :

G-1. A Carnot cycle operates on a working substance between two reservoirs at temperature T_1 and T_2, where $T_1 > T_2$. During each cycle an amount of heat Q_1 is extracted from the reservoir at T_1 and an amount Q_2 is delivered to the reservoir at T_2. Which of the following statements is incorrect ?

(a) Work done in one cycle is $Q_1 - Q_2$

(b) $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

(c) Entropy of the reservoir decreases

(d) Entropy of the universe (consisting of the working substance and the two reservoirs) increases

[GATE-2011]

Soln. The given Carnot engine is shown schematically in the figure aside.

In ideal case (no energy dissipation)

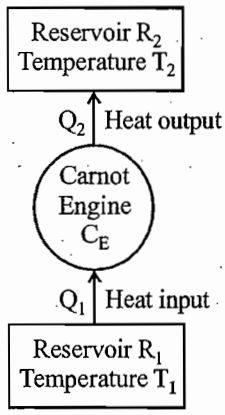
Work done = Heat input – Heat output

$= Q_2 - Q_1$ (a) ...(i)

($\because$ given $T_1 > T_2 \Rightarrow Q_1 > Q_2$)

Now efficiency of a Carnot cycle $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$

$\Rightarrow 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \Rightarrow \boxed{\frac{Q_2}{T_2} = \frac{Q_1}{T_1}}$ (b) ...(ii)



Now, $\Delta S = \frac{dQ}{T}$ (definition of entropy)

Since heat is taken away from R1

$\Rightarrow \Delta S_{R_1} = -\frac{Q_1}{T_1} \Rightarrow$ change in entropy for R_1 is negative

$\Rightarrow$ Entropy of the hotter reservoir decreases (c) ...(iii)

Finally $\Delta S_{universe} = \Delta S_{R_1} + \Delta S_{R_2} + \Delta S_{C_E} = -\frac{Q_1}{T_1} + \left(\frac{Q_1}{T_1} - \frac{Q_2}{T_2}\right) + \frac{Q_2}{T_2}$

$\Rightarrow \boxed{\Delta S_{universe} = 0} \Rightarrow$ (d) is incorrect.

($\Delta S_{universe} = 0$ for reversible process)

Hence, from (i), (ii) and (iii) we find (a), (b) and (c) are correct. Therefore one has to choose option (d) which is incorrect.

Hence, the correct option is (d).

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G-2. A heat pump working on the Carnot cycle maintains the inside temperature of a house at 22°C by suppling 450 kJS^{-1}. If the outside temperature is 0°C, the heat taken, in kJs^{-1}, from the outside air is approximately.

(a) 487 (b) 470 (c) 467 (d) 417

[GATE-2007]

Soln. The efficiency of Carnot heat engine may be defined as $\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$ where, Q_1 is heat taken from the source by working substance and Q_2 is the heat given by working substance to sink respectively, T_1 and T_2 are the temperature of source and sink respectively.

Hence, in question

$Q_1 = 450$ kJ/s, $Q_2 = ?$

$T_1 = 22 + 273 = 295$ K,

$T_2 = 273\ K$

Hence, $\frac{450 - Q_2}{450} = \frac{295 - 273}{295}$ or $Q_2 = \frac{273 \times 450}{295} = 416.44$ kJ/s $\cong 417$ kJ/s

Hence correct option is (d).

Entropy of steam :

Let a small amount of heat dQ be given to 1 gm of water at temperature T. The change in entropy $dS = \frac{dQ}{T}$

If the temp of water rises by dT then $dQ = dT$ $(Q = ms\Delta T)$ S = 1 (for water)

$\therefore \quad dS = \frac{dT}{T} \Rightarrow S = \int dS = \int \frac{dT}{T} = \ell n\, T + A$

A → constant of integration

If we take S = 0 at 0°C(T = 273K) then $A = -\ell n\, 273$

Hence for one gram of water

$S_{water} = \ell n\, T - \ell n\, 273 = \ell n \frac{T}{273}$

The amount of heat needed to convert 1 gm of water into steam at temperature T is L where L = latent heat of vapourization. Hence the increase in entropy $= \frac{L}{T}$

Total entropy of 1 gm of dry saturated steam at temperature T will be

$S_{steam} = S_{water} + \frac{L}{T} = \ell n \frac{T}{273} + \frac{L}{T}$.

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Chapter 4

Maxwell's relations & thermodynamic potentials

Maxwell's thermodynamic relations :

From 1st law of thermodynamics

$$dQ = dU + dW \qquad \ldots (i)$$

where dQ is the amount of heat absorbed in reversible process

The change in entropy is given by

$$dS = \frac{dQ}{T} \qquad \ldots (ii)$$

From eqn (i) & (ii)

$$dU = TdS - PdV$$

So $$\frac{\partial^2 u}{\partial y\,\partial x} = \frac{\partial}{\partial y}\left(T\frac{\partial S}{\partial x} - P\frac{\partial V}{\partial x}\right)$$

$$= T\frac{\partial^2 S}{\partial y \partial x} + \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - P\frac{\partial^2 V}{\partial y dx} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x} = T\frac{\partial^2 S}{\partial y \partial x} - P\frac{\partial^2 V}{\partial y \partial x} + \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x}$$

Thus, $$\frac{\partial^2 U}{\partial x \partial y} = T\frac{\partial^2 S}{\partial x \partial y} - P\frac{\partial^2 V}{\partial x \partial y} + \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} - \frac{\partial P}{\partial x}\frac{\partial V}{\partial y}$$

But $$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y}$$ and $$\frac{\partial^2 S}{\partial x \partial y} = \frac{\partial^2 S}{\partial y \partial x}$$ and $$\frac{\partial^2 V}{\partial x \partial y} = \frac{\partial^2 V}{\partial y \partial x}$$

Hence $$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots (iii)$$

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1st relation : $x = T$ $\quad y = V$

$$\frac{\partial T}{\partial x} = 1 \qquad \frac{\partial V}{\partial y} = 1 \qquad \frac{\partial T}{\partial y} = 0 \qquad \frac{\partial V}{\partial y} = 0$$

Substituting in eqn. (iii) $$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

2nd relation : $x = T$ $\quad y = P$

$$\frac{\partial T}{\partial x} = \frac{\partial P}{\partial y} = 1 \qquad \frac{\partial T}{\partial y} = \frac{\partial P}{\partial x} = 0$$

Substituting in eqn. (iii) $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{1}{T}dQ \quad \Rightarrow \quad \boxed{\left(\frac{dQ}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P}$$

3rd relation : $x = S \qquad y = V$

$$\frac{\partial S}{\partial x} = \frac{\partial V}{\partial y} = 1 \qquad \frac{\partial S}{\partial y} = \frac{\partial V}{\partial x} = 0$$

Substituting in eqn (iii) $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

or $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_V}$

4th relation : $x = S \qquad y = P$

$$\frac{\partial S}{\partial x} = \frac{\partial P}{\partial y} = 1 \quad \text{and} \quad \frac{\partial S}{\partial y} = \frac{\partial P}{\partial x} = 0$$

Substituting in eqn. (iii)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{or} \quad = \boxed{\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial Q}\right)_P}$$

5th relation : $x = P \qquad y = V$ $\quad \frac{\partial P}{\partial x}\frac{\partial V}{\partial S} = 1 \quad \frac{\partial P}{\partial y}\frac{\partial V}{\partial x} = 0$

Substituting in eqn (iii) $\left(\frac{\partial T}{\partial P}\right)\left(\frac{\partial S}{\partial V}\right) - \left(\frac{\partial T}{\partial V}\right)\left(\frac{\partial S}{\partial P}\right) = 1$

6th relation : $x = T \qquad y = S$ $\quad \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} = 1 \quad \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} = 0$

Substituting in eqn. (iii)

$$\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial P}{\partial T}\right)_T \left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial V}{\partial T}\right)_S = 1$$

Helmholtz Function or Helmholtz free Energy (F)

It is also called as thermodynamical potential at constant volume. It is defined by the eqn.

$$F = U - TS$$

Since U, T and S are perfect differentials, F is also a perfect differential. when a system undergoes an infinitesinal reversible change from an initial equilibrium state to a final equilibrium state, the Helmhotz energy changes by an amount given by

$$dF = dU - TdS - SdT \qquad \text{But } dU = TdS - PdV$$
$$= TdS - PdV - TdS - SdT = -PdV - SdT$$

Taking the partial differentiation of F we have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

Since dF is a perfect differential

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{dT}\right) = \frac{\partial}{\partial T}\left(\frac{dF}{\partial V}\right) \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \text{Maxwell's I}^{st} \text{ relation}$$

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Enthalpy or total heat function (H)

(1)

It is defined by $H = U + PV$

when a system undergoes an infinitesinal reversible change from an initial equilibrium state to a final equilibriu (2)
state the enthalpy changes by an amount given by

$dH = dU + PdV + VdP$ But $dU = TdS - PdV$

$dH = TdS - PdV + PdV + VdP = TdS + VdP$

Taking the partial differentiation of H we have

$$\left(\frac{\partial H}{\partial S}\right)_P = T \qquad \left(\frac{\partial H}{\partial P}\right)_S = V$$

(1)

Since dH is a perfect differential we have

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)$$

Or $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ → Maxwell's Fourth relation

Gibbs function or Gibbs free energy (G)

It is also called as thermodynamic potential at constant pressure. It is defined by

$G = H - TS = U + PV - TS$

For an infinitesimal reversible process

$dG = dU + PdV + VdP - TdS - SdT$

$= TdS - PdV + PdV + VdP - TdS - SdT$

$= VdP - SdT$

The partial differentiation of G are

$$\left(\frac{\partial G}{\partial P}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since dG is a perfect differential so we have

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

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Importance :

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(1) Thermodynamic functions are of practical importance in studying the condition of equilibrium of a system eg. The condition of equilibrium for a process in which the temperature and volume of the system remain constant (Isothermal- Isochoric) may be expressed as

$dF = 0 \qquad (\because dF = -PdV - SdT)$

This means that out of various states which a system can assume by isothermal isochoric process, only those are stable in which the Helmholtz free energy ($F = U - TS$) is a minimum

The equation $dF = 0$ refers to a minimum value of F (and not to a maximum value). It follows from the fact that in any natural (irreversible) process the Helmholtz free energy can only fall because the entropy can only increase.

Similarly the condition of equilibrium for a process in which the temperature and pressure of the system remain constant (isothermal isobaric process) may be expressed as

$dG = 0 \qquad (\because dG = VdP - SdT)$

This means that a system at constant temperature and pressure is in stable equilibrium when the Gibbs function G (the thermodynamic potential of constant pressure) is a minimum

Physical significance of Helmholtz free energy : (A Helmholtz free energy)

(1) $A = U - TS \Rightarrow TS = U - A \rightarrow$ Latent energy or bound energy of the system. As it can't be used in useful form (work)

equilibriu (2) For isothermal reversible process

$-dA = PdV = dW$

The Helmholtz free energy is the energy decrease in which (–dA) gives the maximum amount of work (dW) done by the system during an isothermal change from initial state to final state. It is also called thermodynamic potential at constant volume.

$$A = U - TS \Rightarrow A = U + T\left(\frac{\partial A}{\partial T}\right)_V \rightarrow \text{Gibb's- Helmholtz relation}$$

Physical Significance of Enthalpy

(1) $dH = TdS$ (at constant P)

Enthalpy represents the quantity of heat given to the system at constant pressure. So it is called heat contained or total heat function

Physical Significance of Gibbs Function

$dG = VdP - SdT$

$= -dW - SdT + PdV + VdP$

$-dG = dW - PdV$ (For isothermal isobaric process)

Gibbs free energy is such that decrease in it gives the maximum work which can be obtained from the system other than that due to change in volume for isothermal isobaric process. This is also known as thermodynamic potential at constant pressure

$G = H - TS$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \rightarrow \text{Gibb's Helmholtz relation.}$$

Two important derivations.

(i) $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ **(ii)** $\left(\frac{\partial C_P}{\partial P}\right)_T = T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

(i) We Know Maxwell's Relations not given in prior from Maxwell's equation.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

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stem eg. constant

Diffrentiating w.r.t. T at constant volume

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V = \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

hose are

Since for a function of state means II[nd] order differentials are independent of order of differentiation :

fact that an only

$$T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{(multiplying with T on both sides)}$$

remain

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial T}\right)_V\right]_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad (\because dQ = T\,dS)$$

unction

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right) \quad \text{(using definition of } C_v\text{)}$$

(ii) From Maxwell's equation.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Diffrentiating w.r.t. T at constant pressure

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Multiplying both sides by T

$$T\left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial Q}{\partial T}\right)_P\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$ (using definition of C_P).

Q. 50. Establish the following thermodynamic relation

$$\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$$

where α in the coefficient of volume expansion at constant pressure. Hence show that increase in pressure heats a body that expands with rise of temperature and colds that contracts on heating.

Ans. The Maxwell thermodynamic relation is

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying by T both side

$$T\left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial Q}{\partial P}\right)_T = -TV\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$$

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where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ – Coefficient of Volume expansion

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(i) If substance expands with rise in temperature then α will be positive

Hence $\left(\frac{\partial Q}{\partial P}\right)_T = -Ve$

If we increase the pressure, ∂Q at constant temperature will be –Ve, to maintain temperature constant heat must be drawn from the system. It means increase in pressure will heat the system.

(ii) If substance contracts with rise in temperature then α will be negative

$$\left(\frac{\partial Q}{\partial P}\right)_P = +Ve$$

If we increase the pressure $(\partial Q)_T$ will be +ve, to maintain temperature constant heat must be given to the system. It means increase in pressure will cool the system.

Q. 51. Prove the thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and hence prove that $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$.

Ans. The general expression for Maxwell's thermodynamic relation is

$$\left(\frac{\partial T}{\partial Y}\right)_X\left(\frac{\partial S}{\partial X}\right)_Y-\left(\frac{\partial P}{\partial Y}\right)_X\left(\frac{\partial V}{\partial X}\right)_Y=\left(\frac{\partial T}{\partial X}\right)_Y\left(\frac{\partial S}{\partial Y}\right)_X-\left(\frac{\partial P}{\partial X}\right)_Y\left(\frac{\partial V}{\partial Y}\right)_X$$

Let us take $x = T$ $y = V$. we have then

$$\frac{\partial T}{\partial X}=1 \quad \frac{\partial V}{\partial Y}=1 \quad \text{and} \quad \frac{\partial T}{\partial Y}=\frac{\partial V}{\partial X}=0$$

Therefore the general expression reduced to

$$\left(\frac{\partial S}{\partial Y}\right)_x-\left(\frac{\partial P}{dX}\right)_Y=0$$

But $dY = dV$ and $dX = dT$

$$\therefore \quad \boxed{\left(\frac{\partial S}{\partial V}\right)_T-\left(\frac{\partial P}{\partial T}\right)_V=0}$$

Multiplying both sides by T we get

$$T\left(\frac{\partial S}{\partial V}\right)_T=T\left(\frac{\partial P}{\partial T}\right)_V$$

But $TdS = dQ$

$$\therefore \quad \left(\frac{\partial Q}{\partial V}\right)_T=T\left(\partial P/\partial T\right)_V \qquad \text{(1)}$$

Here $dQ \rightarrow$ the heat absorbed at constant temperature

$\therefore$ dQ is the latent heat L

Thus if a body absorbs an amount of heat L (latent heat) to change its state at constant temperature T and specific volumes in the Ist and the 2nd states are V_1 & V_2

eqn. (i) reduces to

$$\frac{L}{V_2-V_1}=T\frac{dP}{dT}$$

or $$\boxed{\frac{dP}{dT}=\frac{L}{T(V_2-V_1)}}$$ → Clausius-Clapeyron eqn.

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Q. 52. What are thermodynamic function (or potential)? Deduce from them the Maxwell's thermodynamic relations. What is the importance of these function ?

Ans. The state of thermodynamic system of constant mass may be specified in terms of the variables P,V,T,U and S between which two thermodynamic relations exist

$$dQ = dU + PdV$$
$$dQ = TdS$$

For a complete description of the behaviour of such system some other relations are required. These relations are mathematically simplified when certain functions of these veriables are introduced.

(i) **Internal energy :** Suppose a system undergoes an infinitesinal reversible change from one equilibrium state to another. The internal energy changes by an amount $dU = dQ - PdV$

$$= TdS - PdV$$

Now taking partial differentiation of dU we get

$$\left(\frac{\partial U}{\partial S}\right)=T \qquad \left(\frac{\partial U}{\partial V}\right)=-P$$

But dU is a perfect differential so we have

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \rightarrow \text{ Maxwell's III}^{rd} \text{ relation}$$

Q. 53. A certain system found to have a Gibb's free energy is given by $G(P,T) = RT\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$, wher
a and R are constants. Find the entropy and specific heat at constant pressure.

Soln. $G(P,T) = RT\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p, \quad S = \frac{5}{2}R - R\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$$

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T\frac{\partial S}{\partial T} = T\left[-R\frac{(RT)^{5/2}}{aP}\cdot\frac{1}{R^{5/2}}\left(\frac{5}{2}\right)T^{3/2}aP\right]$$

$$\boxed{C_p = \frac{5}{2}R}$$

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Problems that appeared in GATE from this section :

G-1. Which among the following sets for Maxwell relation is correct? (U-internal energy, H-enthalpy, A-Helmholtz free energy and G-Gibbs free energy?

(a) $T = \left(\frac{\partial U}{\partial V}\right)_S$ and $P = \left(\frac{\partial U}{\partial S}\right)_V$ **(b)** $V = \left(\frac{\partial H}{\partial P}\right)_S$ and $T = \left(\frac{\partial H}{\partial S}\right)_P$

(c) $P = -\left(\frac{\partial G}{\partial V}\right)_T$ and $V = \left(\frac{\partial G}{\partial P}\right)_S$ **(d)** $P = -\left(\frac{\partial A}{\partial V}\right)_T$ and $S = -\left(\frac{\partial A}{\partial P}\right)_V$

[GATE-2010]

Soln. We have the thermodynamic potentials defined by the following four relations:

(i) $A = U - TS$

(ii) $G = U - TS + PV$

(iii) $H = U + PV$

(iv) $dU = TdS - PdV$

From (i), we get $dA = dU - TdS - SdT$

$= -PdV - SdT$ (using (iv))

$$\Rightarrow \boxed{S = -\left(\frac{\partial A}{\partial T}\right)_V} \quad ...(1)$$

and $\boxed{P = -\left(\frac{\partial A}{\partial V}\right)}$ ...(2)

Now, from (ii), we have

$dG = dU - TdS - SdT + PdV + VdP$ (using (iv))

$= -SdT + VdP$

So, $\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_P}$ ...(3)

and $\boxed{V = -\left(\frac{\partial G}{\partial P}\right)_T}$ ...(4)

Now, from (iii), we have

$dH = dU + PdV + VdP$

$= TdS + VdP$ (using (iv))

So, $\boxed{T = \left(\frac{\partial H}{\partial S}\right)_P}$ ...(5)

and $\boxed{V = \left(\frac{\partial H}{\partial P}\right)_S}$ ...(6)

Now, from (iv) we have

$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V}$ ...(7)

and $\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S}$ ...(8)

From (7) and (8) ; option (a) is wrong

From (5) and (6) ; option (b) is correct

Similarly, from (1), (2), (3) and (4) ; option (c) and (d) are wrong

Hence correct option is (b).

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Chapter 5

Introduction to Statistical Mechanics

Thermodynamics limit :

If $N \to \infty \quad V \to \infty$

Particle density $n = \frac{N}{V}$ is fixed at a preassigned value.

Extensive property : In the thermodynamic limit the properties that become directly proportional to the size of the system (or proportional to the extensive parameters A, N, V, S, E) i.e. $N \to \alpha N$, $V \to \alpha V$ $S \to \alpha S$ then such properties are called extensive properties. They have an additive nature.

Intensive property: In the thermodynamic limit the properties that become independent of the size of the system.

Example: T, P, μ (chemical potential)

Accessible microstate : The microstate which are permitted under the constraints imposed upon the system are called accessible microstate.

Thermodynamic Probability : For a given macrostate the total number of microstate is called thermodynamic Probability of that microstate.

$$S = k_B \log \omega \quad \text{or} \quad S = k_B \log \Omega$$

where ω or $\Omega \to$ Total no. of microstate for a given macrostate (thermodynamic Probability)

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Fundamental Postulate of statistical mechanics (equal a priori a probability) :

For a system in equilibrium all accessible microstate corresponding to a given macrostate are equally probable i.e. probability of finding the system in all microstate for a given macrostate are equal

$$\boxed{S = k_B \log \Omega} \to \textbf{Boltzman entropy probability relation}$$

This eqn. shows the relation between macroscopic & microscopic properties or relation between thermodynamics and statistical mechanics

Random Walk: Let n_1 denote the number of steps to the right and n_2 the corresponding number of steps to the left.

Total number of steps $N = n_1 + n_2$

Net displacement $m = n_1 - n_2 = n_1 - (N - n_1) = 2n_1 - N$ (towards right)

If P = Probability that the step is to the right, $q = 1 - p$ = Probability that step is to the left.

Probability $W_N(n_1)$ of taking (in a total of N steps) n_1 steps to the right and n_2 steps to the left is given by $W_N(n_1) = \frac{N!}{\quad} p^{n_1} q^{n_2}$.

Mean Free Path: Mean free path λ is the average distance traversed by molecule between collisions. Mean free path of a molecule is related to its size, larger its size, shorter its mean free path.

$$\lambda = \frac{1}{\sqrt{2}\,\pi N d^2}$$

where d = diameter of the gas molecule, N = Number of molecules per unit volume.

Q. 54. A system of N particles has only two allowed state A and B. The probability for A is P and for B is 1 – P? What is the probability for the system to be in macrostate defined by the distribution of (r, N – r)?

Ans. The probability of finding r particle in state A = P^r

The probability of finding N – r particle in state B = $(1-P)^{N-r}$

The Total no. of ways in which r particle can be choosen from N – particle is ${}^{N}C_r = {}^{N!}/_{r!(N-r)!}$

The probability in which r particle are in state A and N – r particle in state B is = $\boxed{\frac{N!}{r!(N-r)!}\,P^r\,(1-P)^{N-r}}$

Q. 55. A one dimensional random walker takes step to left or right with equal probability. The probability that the random walker starting from orign is back to orign after N even number of step, is

(i) $\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\left(\frac{1}{2}\right)^N$ (ii) $\frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}$ (iii) $2N!\left(\frac{1}{2}\right)^{2N}$ (iv) $N!\left(\frac{1}{2}\right)^N$

Ans. Probability $P = \frac{N!}{r!(N-r)!}P^r(1-P)^{N-r}$

$$= \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\left(\frac{1}{2}\right)^{\frac{N}{2}}\left(1-\frac{1}{2}\right)^{\frac{N}{2}} = \frac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}\left(\frac{1}{2}\right)^N$$

(i) is correct

Q. 56. Calculate the no. of microstates for a configuration of a system of N distinguishable particles in which there are n_1 particles in a particle state 1 & n_2 particle in state 2, n_3 particle..... n_i particle in the ith state.

Ans. Total No. of particle = N

No. of microstate for state –1 = $N_{C_{n_1}}$

No. of microstate for state –2 = $N - n_{1C_{n_2}}$

No. of microstate for state i^{th} = $N - n_1 - n_2 \ldots n_i - 1\,C_{n_i}$

So total number of microstate is

$$N_{C_{n_1}} \times N - n_1\,C_{n_2} \times N - n_1 - n_2\,C_{n_3} \times \ldots\ldots N - n_1 - n_2 - n_3 - ni - 1\,C_{n_i}$$

$$= \frac{N!}{n_1!(N-n_1)!} \times \frac{(N-n)!}{n_2!(N-n_1-n_2)!} \times \ldots\ldots \frac{(N-n_1-n_2\ldots n_i)!}{n_i!(N-n_1-n_2\ldots n_i)!}$$

$$= \frac{N!}{n_i!(N-n_1-n_2\ldots\ldots n_i)!}$$ – For distinguishable particle

$$= \frac{1}{n_i!(N-n_1-n_2\ldots\ldots n_i!)!} \rightarrow$$ For indistinguishable particle

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Q. 57. Four distinguishable coins are tossed a large no. of time write down the different microstate which may be observed & the macrostate into which they would fall. Give the probability of the most probable macrostate.

Macrostate	Microstate coins having head up	Microstate coins having tail up	No. of microstate	Probability
$n_1 = 4, n_2 = 0$	a b c d	–	1	$\frac{1}{16}$
$n_1 = 3, n_2 = 1$	abc bcd cda dab	d a b c	4	$\frac{4}{16}$
$n_1 = 2, n_2 = 3$	ab ac ad bc bd cd	cd bd bc ad ac ab	6	$\frac{6}{16}$
$n_1 = 1, n_2 = 3$	a b c d	bcd acd abd abc	4	$\frac{4}{16}$
$n_1 = 0, n_2 = 1$		abcd	1	$\frac{1}{16}$

Total no. of microstate = 16

The probability of most probable state = 6/16

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Q. 58. An isolated system consist of two non-interacting Spin $-\frac{1}{2}$ particles a & b fixed in space & kept in magnetic field B. Find out the total no. of microstates allowed to the system.

Ans.	System state or macrostate	Particle state or Microstate		Magnetic moment	energy	no. of microstate
1		U	U	$2\mu_0$	$-2\mu_0 B$	1
2		U	D	0	0	}2
		D	U	0	0	
3		D	D	$-2\mu_o$	$+-2\mu_o B$	1

Total no. of microstate = 4 for Spin $-\frac{1}{2}$ two particle system no. of accessible microstate corresponding to energy.

$E = 0$ is 2.

The no. of microstate for N no. of Spin S particle

$$\boxed{(2S+1)^N}$$

The probability of getting a macrostate in which there are r particle out of N Spin 1/2 particle in spin up state

$$\boxed{{}^{N}C_{r} \times \frac{1}{2^N}}$$

CONTACT BETWEEN STATISTICS & THERMODYNAMICS

A_1	A_2
N_1, V_1, E_1	N_2, V_2, E_2

Now we consider two physical systems A_1 and A_2 which are separately in equilibrium. Let the macrostate of E_1 be represented by parameter N_1, V_1, E_1 so that it has possible microstate $\Omega_1(N_1, V_1, E_1)$

Similarly system A_2 by " " " " N_2, V_2, E_2 " " " " $\Omega_2(N_2, V_2, E_2)$

Now bring the two system into contact with each other through a wall (conducting, rigid & impenetrable) such that N_1, N_2 and V_1, V_2 remain fixed but energies E_1 and E_2 become variable such that

$$E_1 + E_2 = E^0 = \text{constant}$$

The no. of microstate at any time t of the composite system is represented by

$$\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E^0 - E_1) = \Omega(E^0, E_1)$$

The microstate of composite system is also represented by

$$\Omega^0(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2)$$
$$= \Omega_1(E^0 - E_2)\Omega_2(E_2)$$

For maximum Number of microstate $\frac{d\Omega}{dE_1} = 0$

$$\frac{d\Omega}{dE_1} = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2}\frac{\partial E_2}{\partial E_1}$$

$$0 = \Omega_2 \frac{d\Omega_1}{dE_1} - \Omega_1 \frac{d\Omega_2}{dE_2}$$

$$\because E_2 = E^0 - E_1 \quad \therefore \frac{dE_2}{dE_1} = -1$$

$$\boxed{\frac{1}{\Omega_1}\left(\frac{\partial \Omega_1}{\partial E_1}\right)_{N_1, V_1, E_1 = \bar{E}_1} = \frac{1}{\Omega_2}\left(\frac{\partial \Omega_2}{\partial E_2}\right)_{N_2, V_2, E_2 = \bar{E}_2}} \quad \text{(At equilibrium } E_1 \text{ and } E_2 \to \bar{E})$$

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Let $\beta = \left(\frac{\partial \ell n\, \Omega}{\partial E}\right)_{N_1, V_1, E_1 = \bar{E}_1}$

Under equilibrium $\beta_1 = \beta_2$

$$\frac{1}{k_B}\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{k_B T} \quad \text{so} \quad \frac{1}{k_B T_1} = \frac{1}{k_B T_2} \Rightarrow \boxed{T_1 = T_2} \qquad \ldots (1)$$

This is the condition for thermal equilibrium

If the wall is movable and conducting

$$\eta = \frac{1}{k_B}\left(\frac{\partial S}{\partial V}\right) = \frac{1}{k_B}\left(\frac{P}{T}\right)$$

under equilibrium $\eta_1 = \eta_2 \Rightarrow \frac{P_1}{k_B T_1} = \frac{P_2}{k_B T_2}$

for conducting medium $T_1 = T_2 \Rightarrow \boxed{P_1 = P_2}$ ... (2)

Eqn (2) is the condition for mechanical equilibrium and thermal equilibrium.

If the wall is conducting. non-rigid, movable and penetrable

$V_1 + V_2 = V^o \qquad E_1 + E_2 = E^o, \qquad N_1 + N_2 = N^o$ (fixed)

$\beta_1 = \beta_2 \qquad \Rightarrow \qquad T_1 = T_2$

$\eta_1 = \eta_2 \qquad \Rightarrow \qquad P_1 = P_2$

Now, let $\xi = \left(\frac{\partial}{\partial N} \ell n \Omega\right)_{E,V}$

$$\frac{1}{k_B}\left(\frac{\partial S}{\partial N}\right)_{E_1} = -\frac{\mu}{k_B T}$$

$\xi_1 = \xi_2 \qquad \Rightarrow \boxed{\mu_1 = \mu_2}$ (3)

$\mu_1 = \mu_2 \rightarrow$ system is in chemical equilibrium

If $T_1 = T_2, P_1 = P_2$ and $\mu_1 = \mu_2$ then system is thermodynamic equilibrium

Classical ideal gas : Now we discuss the thermodynamical properties of a classical ideal gas composed of N monoatomic (non-interacting) molecule. by statistical method the total no. of ways in which the N- particle can be distributed in the system will be simply equal to the product of the no. of ways in which the individual particles can be distributed in the same space independently of one another volume of phase space

$d\tau = \int d^3x d^3P = \int dx dy dz \int d^3P = V \times \frac{4}{3}\pi P^3$ (6D phase space = 3D position and 3D momentum)

Volume of each phase cell $= h^3$ (∵ particle have 3 degree of freedom)

$\Omega =$ No of microstate $= \frac{\text{Volume of phase space}}{\text{Volume of phase cell}} = \frac{V}{h^3} \frac{4}{3}\pi P^3$

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So $\Omega = \frac{V}{h^3} \frac{\pi P^3}{\frac{3}{4}} = \frac{V}{h^3} \frac{\sqrt{\pi}\,\pi P^3}{\frac{3}{2}!}$ $\left| \sqrt{2} \; 2 \; 2 \; 2 \; \sqrt{\pi} \right.$

$$\Omega = \frac{V}{h^3} \frac{(2\pi ME)^{3/2}}{\left(\frac{3}{2}\right)!}$$

No. of microstate composed of N identical particle

$$\Omega(E) = \left(\frac{V}{h^3}\right)^N \left[\frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!}\right] \rightarrow \text{for sharp energy}$$

If the energy lies between E and E + dE number of microstate

$$\Omega(E+\Delta E) = \Omega(E) + \frac{\partial \Omega}{\partial E}\Delta E \text{ higher terms neglected}$$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!} \quad \frac{3N}{2} E^{\frac{3N}{2}-1} dE$$

Now entropy $S = k_B \log \Omega = k_B \left[\ell n \left(\frac{V}{h^3}\right)^N \frac{(2\pi ME)^{3N/2}}{\left(\frac{3N}{2}\right)!} \right]$

$$S = k_B \left[\ell n \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \ell n \left(\frac{3N}{2}\right)! \right]$$

$$= k_B \left[\ell n \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \left\{ \frac{3N}{2} \ell n \frac{3N}{2} - \frac{3N}{2} \right\} \right]$$

$(\log n! = n \log n - n)$ = Stirliing relation

$$S = k_B \left[\ell n \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \frac{3N}{2} \ell n \frac{3N}{2} + \frac{3N}{2} \right] = k_B \left[\ell n \left(\frac{V}{h^3}\right)^N (2\pi ME)^{3N/2} - \ell n \left(\frac{3N}{2}\right)^{3N/2} + \frac{3N}{2} \right]$$

$$= k_B \left[\ell n \left[\left(\frac{V}{h^3}\right)^N \left(\frac{(2\pi ME)^{3N/2}}{\frac{3N}{2}} \right] \right] \right]$$

$$S = N k_B \ell n \left[\left(\frac{V}{h^3}\right) \left(\frac{4\pi ME}{3N}\right)^{3/2} \right] + \frac{3}{2} N k_B$$

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Equation (1) can also be written as,

$$S = Nk_B \ell n \frac{V}{h^3} + Nk_B \ell n \left(\frac{4\pi ME}{3N}\right)^{3/2} + \frac{3}{2} Nk_B$$

$$Nk_B \ell n \frac{V}{h^3} + \frac{3}{2} Nk_B \left[1 + \ell n (2\pi Mk_B T)\right] \qquad \left(\because E = \frac{3}{2} Nk_B T\right)$$

$$Nk_B \ell n\, V - Nk_B \ell n \left(h^2\right)^{3/2} + \frac{3}{2} Nk_B \left[1 + \ell n (2\pi Mk_B T)\right]$$

$$Nk_B \ell n\, V - \frac{3}{2} Nk_B \ell n\, h^2 + \frac{3}{2} Nk_B \left[1 + \ell n (2\pi Mk_B T)\right]$$

$$\boxed{S = Nk_B \ell nV + \frac{3}{2} Nk_B \left[1 + \ell n \frac{2\pi Mk_B T}{h^2}\right]} \qquad \ldots (2)$$

From equation (1)

$$E(N\,V\,S) = \frac{3h^2N}{4\pi m V^{2/3}} \exp\left[\frac{2S}{3Nk_B} - 1\right]$$

$dQ = TdS = dU + PdV - \mu dN$ ($U = E$ = internal energy $\because$ P.E = 0

$$T = \left(\frac{\partial E}{\partial S}\right)_{NV} = \frac{3h^2N}{4\pi M V^{2/3}} \exp\left[\frac{2S}{3Nk_B} - 1\right]\frac{2}{3Nk_B}$$

$$T = E \times \frac{2}{3Nk_B}$$

$$\boxed{E = \frac{3}{2}Nk_BT = \frac{3}{2}RT}$$

Internal energy of an classical ideal gas $U = \frac{3}{2}k_BT$ specific heat

Specification $C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2}Nk_B$

Pressure : $TdS = dE + PdV - \mu dN$

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,S} = \frac{2}{3}\frac{E}{V}$$

So, $\boxed{PV = \frac{2}{3}E}$

$$PV = \frac{2}{3} \times \frac{3}{2}Nk_BT = Nk_BT$$

$\boxed{PV = Nk_BT = RT}$ → (Ideal gas equation)

$$C_P = \left(\frac{\partial E + PdV}{\partial T}\right)_P = \left(\frac{\partial E + PdV + VdP}{\partial T}\right)_P$$ [$\because$ P = constant dP = 0 so we can add]

dP = 0

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$$C_P = \left[\frac{\partial}{\partial T}(E + PV)\right]_P = \left(\frac{\partial H}{\partial T}\right)_P$$ www.careerendeavour.com

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

$$C_P = \left[\frac{\partial}{\partial T}\left(\frac{3}{2}Nk_BT + Nk_BT\right)\right]_P = \frac{\partial}{\partial T}\frac{5}{2}Nk_BT = \frac{5}{2}Nk_B$$ [$\because E = \frac{3}{2}Nk_BT$, $PV = Nk_BT$ from

$$C_P = \frac{5}{2}Nk_B$$

Now, $\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}Nk_B}{\frac{3}{2}Nk_B} = \frac{5}{3} \Rightarrow \boxed{\gamma = \frac{5}{3}}$

For adiabatic process $PV^\gamma = \text{constant}$

$$\boxed{PV^{5/3} = \text{const}}$$

$$\boxed{TV^{\gamma-1} = TV^{2/3} = \text{const}}$$

$$P = \frac{2}{3}\frac{E}{V} \qquad \frac{E}{V} = \text{energydensity} \qquad dQ = dE + PdV$$

For adiabatic proces $dQ = 0$

$$0 = dE + PdV = d\left(\frac{3}{2}PV\right) + PdV, \qquad 0 = \frac{3}{2}PdV + \frac{3}{2}VdP + PdV$$

$$-\frac{3}{2}VdP = \frac{5}{2}PdV, \qquad \frac{dP}{P} = -\frac{5}{3}\frac{dV}{V}.$$

Integrating both side

$$\ell n\, P = -\frac{5}{3}\ell nV + c = -\ell nV^{5/3} + c$$

$$\ell n\, P + \ell n\, V^{5/3} = c, \quad \ell n\, PV^{5/3} = c$$

$$PV^{5/3} = \text{constant}$$

$(dE)\,\text{adiabatic} = -PdV \qquad (\because dQ = 0$

$$= -\frac{2}{3}\frac{E}{V}dV \qquad S = Nk_B\ell n\left[\frac{V}{h^3}\left(\frac{4\pi ME}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk_B$$

Replace $N = \alpha N$, $V = \alpha V$ and $E = \alpha E$ and if $S = \alpha S$

Then S is an extensive property

$$= (\alpha N)\,k_B\,\ell n\left[\frac{\alpha V}{h^3}\left(\frac{4\pi M\alpha E}{3N\alpha k_B}\right)^{3/2}\right] + \frac{3}{2}N\alpha k_B \neq \alpha S$$

Since entropy doesn't satisfy the extensive property (additive). So we have to modify

Entropy of mixing : The entropy of mixing is defined as

$$\Delta S = S_T - \sum_{i=1}^{N} Si, \qquad S_T = \text{Entropy after mixing, } Si = \text{Entropy before mixing of individual system}$$

The entropy of an ideal gas given by

$$S = Nk_B\,\ell n\, V + \frac{3}{2}Nk_B\left[1 + \ell n\left(\frac{2\pi mk_BT}{h^2}\right)\right]$$

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Entropy is not an extensive quantity of the system i.e if we increase the extensive parameter by a factor α, keeping the intensive variable unchanged then the entropy of the system which should also increase by same factor α doesn't increase. The entropy of an ideal gas is not extensive due to the term ℓnV. This means that entropy of the system is different from the sum of the entropies of its parts. This is called **Gibbs paradox**. Gibbs visualised the mixing of two ideal gas (1) and (2) both being initially at the same temperature T. The temperature remain same after mixing and before mixing

$$\sum_{i-1}^{2} N_i\,k_B\ell nV_i + \frac{3}{2}N_ik_B\left[1 + \ell n\left(\frac{2\pi m_ik_BT}{h^2}\right)\right]$$

$$= N_1k_B\,\ell nV_1 + \frac{3}{2}N_1k_B\left[1 + \ell n\left(\frac{2\pi m_1k_BT}{h^2}\right)\right] + N_2k_B\,\ell n\,V_2 + \frac{3}{2}N_2k_B\left[1 + \ell n\left(\frac{2\pi m_2k_BT}{h^2}\right)\right]$$

Entropy after mixing $\rightarrow$ $N = N_1 + N_2$ $\quad V = V_1 + V_2$

$$S_T = (N_1 + N_2)\, k_B\, \ell n\, (V_1 + V_2) + \frac{3}{2}(N_1 + N_2) k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

Here $m_1 = m_2 = m$

Entropy of mixing

$$\Delta S = S_T - \sum_{i=1}^{2} Si = (N_1 + N_2)\, k_B \ell n\, (V_1 + V_2) + \frac{3}{2}(N_1 + N_2) k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$- N_1 k_B\, \ell n\, V_1 - \frac{3}{2} N_1 k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right] - N_2 k_B\, \ell n\, V_2 - \frac{3}{2} N_2 k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$= (N_1 + N_2)\, k_B\, \ell n\, (V_1 + V_2) - N_1\, k_B\, \ell n\, V_1 - N_2 k_B\, n\, V_2$$

$$= \left[N_1\, k_B\, \ell n\, (V_1 + V_2) - N_1\, k_B\, \ell n\, V_1\right] + \left[N_2\, k_B\, \ell n\, (V_1 + V_2) - N_2\, k_B\, n\, V_2\right]$$

$$\Delta S = N_1 k_B\, \ell n\, \frac{V_1 + V_2}{V_1} + N_2 k_B\, \ell n\, \frac{V_1 + V_2}{V_2}$$

Since $\frac{V_1 + V_2}{V_1} > 1$ or $\frac{V_1 + V_2}{V_2} > 1$

So $\Delta S > 0$

If, initial density = density of mixture i.e. $\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1 + N_2}{V_1 + V_2}$

$$\Delta S = k_B \left[N_1\, \ell n \frac{N_1 + N_2}{N_1} + N_2\, \ell n \frac{N_1 + N_2}{N_2}\right]$$

$\Delta S = > 0$

If we consider the mixing of two same gas with a common initial temperature T and a common initial particle density n (reversible process) we get

$\Delta S = > 0$

But for reversible process $\Delta S = > 0$

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Thus once again we are led to believe that there is something basically wrong with that expression. To avoid the paradoxial situation Gibbs diminished entropy(S) by an another term $k_B\, \ell n\, N!$, S_1 by $k_B\, \ell n\, N_1!$ and S_2 by $k_B\, \ell n\, N_2!$

$$S = N k_B\, \ell n\, V + \frac{3}{2} N k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right] - k_B\, \ell n\, N!$$

$$= N k_B\, \ell n V + \frac{3}{2} N k_B \left[1 + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right] - N k_B\, \ell n\, N + N k_B$$

$$S = N k_B\, \ell n \frac{V}{N} + \frac{3}{2} N k_B \left[\frac{5}{2} + \ell n\left(\frac{2\pi m k_B T}{h^2}\right)\right] \rightarrow \text{Sackur Tetrode eqn.}$$

By replacing E by αE, V by αV and N by αN we get αS instead of S. So, S is an extensity property

Chemical Potential :

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V,S} = E\left[\frac{S}{3N} - \frac{2S}{3N^2 k_B}\right] = k_B T \ell n \left(\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right)$$

Gibb's free energy :

$$G = \mu N = N k_B T \ell n \left[\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right] \quad G = E + PV - TS, \quad A = E - TS = G - PV$$

Helmholtz free energy :

$$\text{So } A = N k_B T \left[\ell n \left\{\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2}\right\} - 1\right]$$

A is an extensive property while μ is an intensive property of the system.

Q. 59. We have equal amount of two identical ideal gases at the same temperature T but at different pressure P_1 and P_2 in two containers of volume V_1 and V_2 respectively. The containers are connected. Find the change in entropy. (The temperature after mixing also remains same)

Ans.

$$S = N k_B \ell n \left(\frac{V}{N}\right) + \frac{3}{2} N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$\sum_{i=1}^{2} Si = N_1 k_B \ell n \frac{V_i}{N} + \frac{3}{2} N_1 k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$= N k_B \ell n \frac{V_1}{N} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right] +$$

$$= N k_B \ell n \frac{V_2}{N} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

$$\begin{cases} P_1 V_1 = N k_B T \Rightarrow \dfrac{V_1}{N} = \dfrac{k_B T}{P_1} \\ P_2 V_2 = N k_B T \Rightarrow \dfrac{V_2}{N} = \dfrac{k_B T}{P_2} \end{cases}$$

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$$\sum_{i=1}^{2} Si = N k_B \ell n \frac{k_B T}{P_1} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right] +$$

$$N k_B \ell n \frac{k_B T}{P_2} + \frac{3}{2} N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

Total entropy :

$$S_T = 2N k_B \ell n \frac{V_1 + V_2}{2N} + \frac{3}{2} \times 2N k_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

Change in entropy

$$\Delta S = S_T - \sum_{i=1}^{2} Si = 2N k_B \ell n \frac{V_1 + V_2}{2N} - N k_B \ell n \frac{k_B T}{P_1} - NK \ell n \frac{k_B T}{P_2}$$

Let after mixing pressure = P and after mixing total No of particle = N + N = 2N

$$P(V_1 + V_2) = 2N k_B T \qquad P(V_1 + V_2) = 2N k_B T$$

$$\frac{(V_1+V_2)}{2N}=\frac{k_BT}{P}$$

$$\frac{1}{P}=\frac{V_1+V_2}{2Nk_BT}=\frac{V_1}{2Nk_BT}+\frac{V_2}{2Nk_BT}$$

$$\Delta S=2Nk_B\,\ell n\frac{k_BT}{P}-Nk_B\,\ell n\frac{k_BT}{P_1}-Nk_B\,\ell n\frac{k_BT}{P_2}$$

$$\frac{1}{P}=\frac{1}{2}\left(\frac{1}{P_1}+\frac{1}{P_2}\right)$$

$$=Nk_B\,\ell n\left(\frac{k_BT}{P}\right)^2-Nk_B\,\ell n\frac{k_BT}{P_1}-Nk_B\,\ell n\frac{k_BT}{P_2}$$

$$P=\frac{2P_1P_2}{P_1+P_2}$$

$$=Nk_B\,\ell n\frac{\left(\frac{k_BT}{P}\right)^2}{\left(\frac{k_BT}{P_1}\right)\left(\frac{k_BT}{P_2}\right)}$$

$$=Nk_B\,\ell n\left[\frac{(k_BT)^2(P_1+P_2)^2}{(2P_1P_2)^2}\times\frac{P_1P_2}{(k_BT)^2}\right]$$

$$\Delta S=Nk_B\,\ell n\frac{(P_1+P_2)^2}{4P_1P_2}$$

$$\boxed{\Delta S=Nk_B\,\ell n\frac{(P_1+P_2)^2}{4P_1P_2}}$$

Here we get $\Delta S>0$

(We are considering identical particle. So it is a reversible case only when the particle density is same otherwise for identical gas also we will get $\Delta S>0$.)

PHASE SPACE

Phase Space: $d\tau=dx\,dy\,dz\,dP_x\,dP_y\,dP_z$

$=dxdP_x\,dydP_y\,dzdP_z=h.h.h=h^3$

Volume of phase cell $=h^{3N}=h^f$

Dimension of phase space = 2f (f degree of freedom). If f is the degree of freedom of a single particle and N is the total no. of particle, then dimension of phase space is = 2Nf

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No. of microstate in phase space $=\frac{\text{Total Volume of Phase Space allowed to the system}}{\text{Volume of phase Cell }(h^3)}$

Q. 60. Calculate the number of microstate for a free particle in 3-dimension that have momentum p.

Ans. $d\tau=dx\,dy\,dz\,dp_x\,dp_y\,dp_z$

Allowed Phase Space Volume $=\int d\tau=\int dxdydz\int dp_xdp_ydp_z$

$$=V\int p^2dp\int_0^{\pi}\sin\theta dq\int_0^{2\pi}d\phi=V\frac{4}{3}\pi p^3$$

No. of microstate $=\frac{V}{h^3}\times\frac{4}{3}\pi p^3$

Note : for 2. dimension.

$$\int dx = \int dx \int dy \int dp_x \int dp_x$$

$$= \int d^2q \, . \, d^2p \qquad = A.\pi p^2 \quad \{\text{where} A = \text{area}\}$$

Since wave polarize in 2 dimension

$$\int dr = 2A\pi p^2$$

If momentum lies between p and p + dp

$$\therefore \text{ No. of microstate} = \frac{2A}{h^2} 2\pi p dp = \frac{4A\pi}{h^2} pdp$$

If momentum lies between p and p + dp then no. of microstate $= \frac{V}{h^3} 4\pi p^2 dp$

$$\text{Density of state} = \frac{\text{no. of state}}{\text{Volume}} \text{ or } \frac{\text{no. of state}}{\text{energy int erval}}$$

PHASE – SPACE DIAGRAM

Problems that appeared in GATE from this section :

G-1. The phase diagram of a free particle of mass M and K.E, E moving in one-dimensional box with perfectly elastic walls at x = 0 and x = L is given by **[GATE-2006]**

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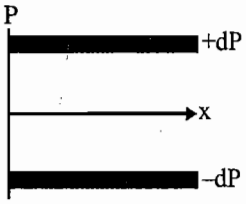
Soln. For free particle momentum P_x is doubly degenerate. For each energy E

$$\frac{P^2}{2M} = E \Rightarrow P = \pm\sqrt{2mE}$$

Which is independent of x but x can only be +ve between 0 to L.

Hence correct option is (a).

- If there would be some range for E from E to E + dE instead of sharp values.

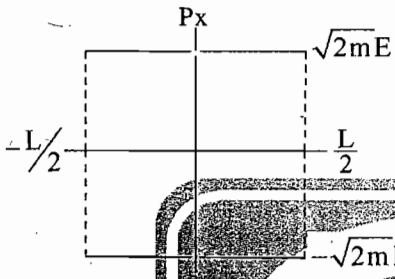


$$E = \frac{P^2}{2m} \Rightarrow P^2 = 2mE \Rightarrow P = \sqrt{2mE}$$

$$dP = \frac{1}{2\sqrt{2mE}} 2m\, dE$$

$$dP = \frac{mdE}{\sqrt{2mE}}$$

- If the origin of phase space is the origin of box



For the above problem we now calculate the no. of phase cell or accessible microstate. If $\bar{E}$ lies between E and E + dE

As it is 1 dimension case the area of phasecell in phase space is

$$\delta x\, \delta P_x = h$$

$2L\, dP_x \rightarrow$ this is area of region accessible to free space

$$2L\, d\left(\sqrt{2mE}\right) = 2L \times \frac{1}{\sqrt{2mE}} 2m\, dE = \sqrt{2m}\, L E^{-1/2} dE$$

Density of state g(E)= number of states per unit energy range

$$= \frac{L(2M)^{1/2} E^{-1/2}}{h}$$

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G-2. The dimension of phase space of ten rigid diatomic molecules is:

(a) 5 **(b) 10** **(c) 50** **(d) 100**

[GATE-2004]

Soln. A rigid diatomic molecule ⇒ degree of function = 5 so, each molecule will require total 5 coordinate variables and 5 momentum variables for their complete description (3-translational, 2-rotational). Hence, each molecule requires 10 phase space dimensions.

∴ Total dimension of 10 such molecules in the phase space = 10 × 10 = 100.

Hence correct option is (d).

(5 degree of freedom for a rigid diatomic molecule can also be understood by the fact that there are 2 particles each with 3 degree of function but there is one constraint that being rigid, the distance between them is fixed, therefore, total degree of function = 3 + 3 – 1 = 5).

PHASE SPACE DIAGRAM OF AN OSCILLATOR

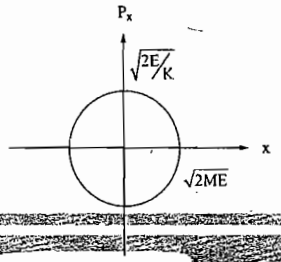
Energy of a one dimensional harmonic oscillator whose position co-ordinate is x and momentum co-ordinate is P_x is given by

$$E = \frac{P_x^2}{2m} + \frac{1}{2}Kx^2 \qquad K = m\omega^2 \qquad \omega = \text{angular frequency}$$

Where the 1st term is the K.E and the 2nd term is P.E. What is the trajectory of oscillator in phase space?

Q. 61. Find the accessible region & the no. of accessible microstate of oscillator?

Ans. $E = \frac{P_x^2}{2m} + \frac{1}{2}Kx^2$ or $\frac{P_x^2}{2mE} + \frac{Kx^2}{2E} = 1$



$$\frac{Px^2}{\left(\sqrt{2mE}\right)^2} + \frac{x^2}{\left(\sqrt{\frac{2E}{K}}\right)^2} = 1 \qquad \ldots (1)$$

For constant energy E eqn. (1) describes an ellipse in phase space i.e. x – p plane

The phase points are those lying on the elliptical path having a semimajor axis $\sqrt{2mE}$ and semiminor axis $\sqrt{\frac{2E}{K}}$

At any particular instant the phase space of the oscillator is represented by some point on the ellipse.
The area of the ellipse in phase space is πab where a is the semimajor axis and b is the semiminor axis.

$$A = \pi ab = \pi\sqrt{2mE}\sqrt{\frac{2E}{K}} = 2\pi E\sqrt{\frac{m}{K}} = \frac{2\pi E}{\omega}$$

It represents the phase space available to the oscillator having energy between o & E or this is the accessible region.

Now the accessible no. of microstates $= \frac{\text{Area of accessible region}}{\text{Area of a point in phase space (i.e cell)}}$

$$= \frac{2\pi E}{\omega h} = \frac{E}{\omega\hbar}$$

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The phase space available to the oscillator having energy between E and E + dE is

$$dA = 2\pi\sqrt{\frac{m}{K}}\,dE = \frac{2\pi}{\omega}dE$$

Q. 62. Calculate the number of microstates accessible to the photon having frequency between υ and $\upsilon + d\upsilon$ confined to a 3 dimentional cavity of volume V.

Ans. No. of microstate in frequency range 0 to υ

$$\Omega = \frac{V}{h^3}\frac{4}{3}\pi\left(2mE\right)^{3/2} \qquad E = \frac{P^2}{2m} \Rightarrow P = \sqrt{2mE}$$

$$= \frac{V}{h^3}\frac{4}{3}\pi\left(P^2\right)^{3/2} \qquad P = \frac{E}{C} = \frac{h\upsilon}{C}$$

$$\Omega = \frac{V}{h^3}\frac{4}{3}\pi\ P^3 = \frac{V}{h^3}\frac{4}{3}\pi\left(\frac{h\upsilon}{c}\right)^3 = \frac{4}{3}\frac{\pi V\upsilon^3}{c^3}$$

No. of microstates in the frequency range υ and $\upsilon + d\upsilon$ is

$$d\Omega = \frac{4}{3}\frac{\pi V}{c^3}3\upsilon^2\, d\upsilon = \frac{4\pi V}{c^3}\upsilon^2 d\upsilon$$

Density of state

$g(E)$ = no. of states per unit energy range

we have $\Omega = \frac{V}{h^3}\frac{4}{3}\pi(2mE)^{3/2}$

$$d\Omega = \frac{V}{h^3}\frac{4}{3}\cdot\frac{3}{2}\pi(2mE)^{1/2}\,2m\,dE$$

$$= \frac{V}{h^3}.2\pi(2m)^{3/2}E^{1/2}\,dE$$

$$\left[E = \frac{P^2}{2m} \Rightarrow 2m = \frac{P^2}{E} = \frac{E^2}{c^2E} = \frac{E}{c^2}\right]$$

$$= \frac{V}{h^3}2\pi\left(\frac{E}{c^2}\right)^{3/2}E^{1/2}\,dE$$

$$= \frac{V}{h^3}\frac{2\pi}{c^3}E^2\,dE$$

$$g(E) = \frac{d\Omega}{dE} = \frac{2\pi VE^2}{h^3c^3}$$

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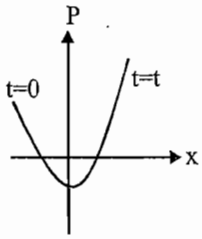
Chapter 6

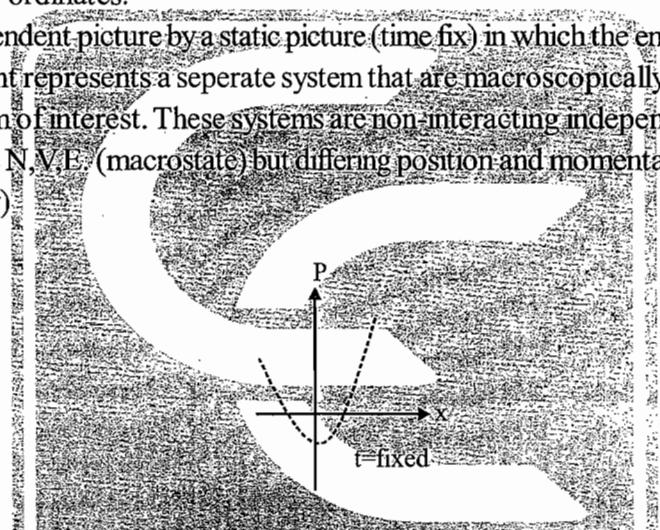
Ensembles in Statistical Physics

The description of any system in statistical physics is done by considering ensembles. Once we know our ensemble (collection of systems etc.), we can quickly apply the laws of statistical mechanics to it and understand the physics thereof.

Part of phase line constructed due to the motion of phase point with time. Each phase point on the line corresponds to different time co-ordinates.

Gibbs replace this time dependent picture by a static picture (time fix) in which the entire phase line exists at one time. Then each phase point represents a seperate system that are macroscopically identical but microscopically different to the system of interest. These systems are non-interacting independent system. All members are identical in features like N,V,E. (macrostate) but differing position and momenta co-ordinates of individual molecules (microscopically)





A collection of large no. of independent systems which are macroscopically identical but microscopically different is called ensemble.

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The concept of ensemble helps in understanding the actual system more completely. It represents at one time the microstate of actual system which would occur in the course of time. We study the statistical behaviour of the ensemble by the knowledge of the behaviour of the ensemble we can predict the probable behaviour of the system under consideration.

1. **Microcanonical ensemble (N, V, E) :**
The ensemble in which all element have same macrostate represented by same no. of particle N, same volume V and same energy E i.e. macrostate is specified by (N,V, E) for all elements (systems). All elements of microcanonical ensemble are separated by impenetrable, rigid and non-interacting walls such that values of (N, V, E) for a particular system are not effected by the presence of other system i.e. all systems are isolated to each other.

2. **Canonical ensemble (N, V, T) :** The ensemble in which all elements will have same macrostate represent by same N,V, T for all elements. The elements of a canonical ensemble are separated from each other by inpenterable, rigid and conducting walls such that the values of N, V, T for a particular system are not effected by others. In canonical ensemble each element is in thermal contact (equilibrium) with heat reservoir or with all other elements of the ensemble at temp T. In this ensemble elements can exchange energy but not particle.

3. **Grand canonical ensemble (μ, V, T):** The ensemble in which all elements will have same macrostate represent by same μ, V, T for all elements. The elements of a canonical ensemble are separated from each other by impenetrable, rigid and conducting walls such that the values of μ, V, T for a particular system aren't affected by others. In this ensemble the elements are in contact with particle energy reservoir. The elements can exchange energy as well as particle.

MICROCANONICAL ENSEMBLE

Microcanonical ensemble: For microcanonical ensemble energy remains constant (systems are isolated)

Density Function s: The density function gives the idea of no. of representative points lying in the region allowed to the system.

$$\rho(q,p) = \rho(E) = \text{constant} \qquad \{\text{sharp value}\}$$

we may prefer to specify a range of energy value $\left(E-\frac{1}{2}\Delta\right)$ to $\left(E+\frac{1}{2}\Delta\right)$ rather than a sharply defined value of E. Accordingly the representative points of the ensemble have a choice to lie anywhere within a hypershell defined by the condition.

$$\rho(q,p) = \text{constant if} \qquad E-\frac{1}{2}\Delta < H(p,q) < E+\frac{1}{2}\Delta$$

$$= 0 \qquad \text{Otherwise}$$

Accordingly the expectation value of any varible f(q, p) is given by

$$\langle f(q,p)\rangle = \frac{\int f(q,p)\rho(q,p)\,d\omega}{\int \rho(q,p)\,d\omega}$$

$d\omega = d^{3N}q\ d^{3N}p$ = volume element in phase space

Since $\rho(q,p)$ is constant

$$\langle f(q,p)\rangle = \frac{\int f(q,p)\,d\omega}{\int d\omega}$$

The expectation value of representative points lying in a volume element $d\omega$ of the relevent hypershell is simply proportional to volume element $d\omega$. In otherwords that a prior probability of finding a representative point in a given volume element is equal to the probability of finding a representative point in an equibalent volume element $d\omega$ located anywhere in the hypercell. This is the postulate of equal a priory probability of representative points or microstate.

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Stationary ensemble :

1. The ensemble for which density function is constant is called stationary ensemble (M.C)

2. If $\frac{\partial S}{\partial t} = 0$ for an ensemble then that ensemble is called stationary ensemble (microcanonical)

Ensemble average of any physical quantity is identical with the value on excepts to obtain on making an appropriate measurement on the given system.

The thermodynamics of the system in microcanonical ensemble would than be discussed by calculating the no. of microstate in accessible regions

$$\Omega = \frac{\text{Volume of accessible region in phase space}}{\text{Volume of phase cell}}$$

$$\Omega = \frac{w}{w_0} \quad \text{where, } w_0 = h^f,\ f - \text{degree of freedom}$$

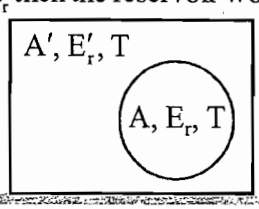
CANONICAL ENSEMBLE

In canonical ensemble, the energy E of a system become variable and can take values from 0 to ∞.

Equilibrium between a system and a heat reservoir :

We consider the given system A, immersed in a very large heat reservoir A′. In the equilibrium both the system and the heat reservoir would have the common temp T. Their energies however would be variable and could have at any time t values lying anywhere between 0 and E°

$\left[\text{E} = \text{energy of A}\left(\text{E}_r\right) + \text{energy of A}'\left(\text{E}_r'\right)\right]$. If at any particular instant of time the system A happens to be in a state characterised by the energy E_r then the reservoir would have energy E_r'.



Such that $\text{E}_r + \text{E}_r' = \text{E}^\circ = \text{constant}$ Since the reservoir is much larger than the given system

So $\text{E}_r << \text{E}^\circ \quad \frac{\text{E}_r}{\text{E}_o} = \frac{\text{E}_o - \text{E}_r'}{\text{E}_o} = \left(1 - \frac{\text{E}_r'}{\text{E}_o}\right) << 1$

with the state of the system E, the reservoir can still be in any one of the large no. of states compatible with the energy E_r'. Let the no. of states be denoted by $\Omega'\left(\text{E}_r'\right)$ The larger the number of states available to the reservoir the larger probability of the reservoir assuming that particular energy value E_r'. Since the various possible states are equally likely to occour the relevant probability would be directly proportional to this number

$$\text{P}_r \alpha\, \Omega'\left(\text{E}_r'\right) \simeq \Omega'\left(\text{E}^{(0)} - \text{E}_r\right)$$

$$\text{P}_r = \text{c}\ \Omega'\left(\text{E}^{(0)} - \text{E}_r\right) \Rightarrow \ell\text{n}\,\text{P}_r = \ell\text{n}\,\Omega'\left(\text{E}^{(0)} - \text{E}_r\right) + \ell\text{n}\,\text{C}$$

Expanding the series about $\text{E}_r = 0$ and $\text{E}_r' = \text{E}^{(0)}$

(Formula used $f(a+h, b+K) = f(a,b) + \frac{\partial f}{\partial x}h + \frac{\partial f}{\partial y}K + \frac{1}{2!}\left(h\frac{\partial}{\partial x} + K\frac{\partial}{\partial y}\right)^2 f\,|a,b + \ldots\ldots$ Taylor series expansion)

$$\ell\text{n}\,\text{P}_r = \ell\text{n}\,\Omega'\left(\text{E}_r'\right) + \ell\text{n}\,\text{C} = \ell\text{n}\,\Omega'\left(\text{E}_r' + \text{E}^{(0)} - \text{E}^{(0)}\right) + \ell\text{n}\,\text{C}$$

$$\text{E}_r' - \text{E}^{(0)} = \text{h} \quad \text{and} \quad \text{E}^{(0)} = \text{a}$$

$$\ell\text{n}\ \text{P}_r = \ell\text{n}\,\Omega'\left(\text{E}_r'\right)\text{E}_r' = \text{E}^{(0)} + \left(\text{E}_r' - \text{E}^{(0)}\right)\frac{\partial}{\partial \text{E}_r'}\ell\text{n}\,\Omega'\left(\text{E}_r'\right)\Big|_{\text{E}_r' = \text{E}^{(0)}} + \ell\text{n}\,\text{C}$$

$$\ell\text{n}\,\text{P}_r = \ell\text{n}\,\text{K} + \frac{\partial}{\partial \text{E}_r'}\ell\text{n}\,\Omega'\left(\text{E}_r'\right)\Big|_{\text{E}_r' = \text{E}^{(0)}} + \ell\text{n}\,\text{C}$$

$$\ell\text{n}\text{K} + \ell\text{n}\,\text{C} = \ell\text{n}\text{K}'$$

$$\ell\text{n}\,\text{P}_r = \ell\text{n}\,\text{K} + \frac{\partial}{\partial \text{E}_r'}\ \ell\text{n}\,\Omega'\left(\text{E}_r'\right)\Big|_{\text{E}_r' = \text{E}^{(0)}} \times \left(-\text{E}_r\right)$$

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$$\ell n\, P_r = \ell n\, K - \beta E_r$$

$$P_r = K\, e^{-\beta E_r} \quad \text{or} \quad \boxed{P_r \propto e^{-\beta E_r}}$$

$$\sum_r P_r = K \sum_r e^{-\beta E_r} \Rightarrow 1 = K \sum_r e^{-\beta E_r}$$

$$K = \frac{1}{\sum_r \text{exP}^{-\beta E_r}} \Rightarrow P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}$$

The partition function indicates that how the particles are partitioned among the various energy states of the system.

If the level have multiplicity or degeneracy or statistical weight g_r then

$$P_r = \frac{g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$$

Partition function for quantum mechanical system (energy discontinuous)

$$\boxed{Q_N(V,T) = \sum_r g_r e^{-\beta E_r}}$$

Partition function for classical distinguishable system

$$Q_N(V,T) = \frac{1}{h^{3N}} \int e^{-\beta E_r} d^3p\; d^3q$$

Partition function for semiclassical indistinguishable system

$$Q_N(V,T) = \frac{1}{h^{3N}} \frac{1}{N!} \int e^{-\beta E_r} d^3p\, d^3q$$

$$Q_N(V,T) = [Q_1(V,T)]^N \text{ distinguishable}$$

$$= \frac{[Q_1(V,T)]^N}{N!} \text{ indistinguishable}$$

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Q. 63. Show that the partition function of two independent (non-interacting) system i and j is given by

$$Z_{ij} = Z_i \times Z_j$$

Ans. We know that

$$P_i = \frac{e^{-\beta E_i}}{Z_i},\; P_j = \frac{e^{-\beta E_j}}{Z_j}$$

$$E = E_i + E_j,\; P_{ij} = \frac{e^{-\beta(E_i + E_j)}}{Z_{ij}}$$

$$P_{ij} = \frac{e^{-\beta E}}{Z_{ii}} = \frac{e^{-\beta(E_i + E_j)}}{Z_{ii}} = \frac{e^{-\beta E_i} \times e^{-\beta E_j}}{Z_{ij}}$$

$$P_{ij} = P_i \times P_j$$

$$\frac{e^{-\beta E_i} \times e^{-\beta E_j}}{Z_{ij}} = \frac{e^{-\beta E_i}}{Z_i} \times \frac{e^{-\beta E_j}}{Z_i}$$

So $Z_{ij} = Z_i \times Z_j$

In general $Z_{ijK}.....= Z_i \times Z_j \times Z_k \times .....$

Total partition function $Z = Z_{\text{Rotational motion}} \times Z_{\text{Translational motion}} \times Z_{\text{Vibrational motion}} \times .....$

Q. 64. A system consist of three independent particles localised in space. Each particle have two states of energy O and E. When the system is in thermal equilibrium with a heat bath at temperature T. Calculate its partition function ?

Ans. Method :–1

$$Q_N(V,T) = \sum_r g_r e^{-\beta E_r}$$

$$Q_1(V,T) = \sum e^{-\beta E_r} = 1 + e^{-\beta E} \quad (\text{put } E_r = 0 \text{ \& } E)$$

Or $$Q_3(V,T) = [Q_1(V,T)]^3 = (1+e^{-\beta E})^3 = 1 + e^{-3\beta E} + 3e^{-2\beta E} + 3e^{-\beta E}$$

State No.	Energy State	Total Energy	Degeneracy
	0		
1	abc	0	1 g_1
2	c	E	
	bc	a E	3 g_2
	ca	b E	
3	a	bc 2 E	
	b	ca 2 E	3 g_3
	c	ab 2 E	
4	0	abc 3 E	1 g_4

$$Q_N(V,T) = \sum_r g_r e^{-\beta E_r}$$

$$= g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3} + g_4 e^{-\beta E_4}$$

$$= 1 + 3e^{-\beta E} + 3e^{-2\beta E} + e^{-3\beta E}$$

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Q. 65. The partition function for two Bose particle each of which can occupy any of the energy level 0 and E

i) $1 + e^{-2E/KT} + 2e^{-E/KT}$ ii) $1 + e^{-2E/KT} + e^{-E/KT}$

iii) $2e^{-2E/KT} + e^{-E/KT}$ iv) $e^{-2E/KT} + e^{-E/KT}$

Ans.	0	E	Total energy	degeneracy
1	aa	0	0	1 (g_1)
2	a	a	E	1 (g_2)
3	0	a	2 E	1 (g_3)

$$Q_N(V,T) = \sum_r g_r e^{-\beta E_r} = g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + g_3 e^{-\beta E_3}$$

$= 1 + e^{-\beta E} + e^{-2\beta E}$

$\therefore$ (ii) is correct

Q. 66. The partition function of single gas molecule is $Z\alpha$. The partition function of N such non-interacting gas molecule is given by

i) $\frac{(Z\alpha)^N}{N!}$ ii) $(Z\alpha)^N$

iii) $N\,Z\alpha$ iv) $(Z\alpha)^N / N$

Ans. For indistinguishable particle $\frac{(Z\alpha)^N}{N!}$

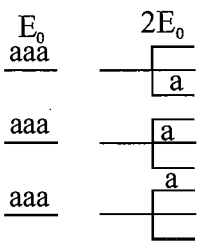
for distinguishable particle $(Z\alpha)^N$

Q. 67. A system has energy level E_0, $2E_0$, $3E_0$..... where the excited state are triply degenerate. Four non- interacting Bosons are placed in this system. If the total energy of these Bosons is $5E_0$. The number of microstate is

1) 2 ii) 3 iii) 4 iv) 5

Ans. Total energy $= 5E_0$

For this 3 bosons must be in E_0 state and 1 in $2E_0$ state.



(ii) Option is correct.

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Q. 68. An ensemble of quantum harmonic oscillator is kept at a finite temperature T

$T = \frac{1}{k_B \beta}$ **k_B – Boltzmann constant**

The partition function of a single oscillator with energy $\left(n + \frac{1}{2}\right)\hbar\omega$ is given by

(i) $Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$ (ii) $Z = \frac{e^{-\beta\hbar\omega/2}}{1 + e^{-\beta\hbar\omega}}$

(iii) $Z = \frac{1}{1 - e^{-\beta\hbar\omega}}$ (iv) $Z = \frac{1}{1 + e^{-\beta\hbar\omega}}$

Ans. (i) $Q_N(V_i\,T) = \sum_r e^{-\beta E} = \sum_n e^{-\beta\left(n+1/2\right)\hbar w}$

$= e^{-\beta\hbar\omega/2} + e^{-3/2\beta\hbar\omega} + e^{-5/2\beta\hbar\omega} + ...$

$= e^{-\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + e^{-\beta\hbar\omega} + ...$

$= e^{-\beta\hbar\omega/2}\left(\frac{1}{1-e^{-\beta\hbar\omega}}\right)$ use G.P, formula $\left\{\begin{array}{ll} R = 1 + r + \pi^2 ..... \infty & \text{G.P.} \\ \sum_0^\infty R = \frac{1}{1-r} & r < 1 \end{array}\right\}$

Q. 69. The average number of energy quanta of the oscillator is given by

(i) $\langle n\rangle = \frac{1}{e^{\beta\hbar\omega} - 1}$ (ii) $\langle n\rangle = \frac{e^{-\beta\hbar\omega}}{e^{\beta\hbar\omega} - 1}$

(iii) $\langle n\rangle = \frac{1}{e^{\beta\hbar\omega} + 1}$ (iv) $\langle n\rangle = \frac{e^{-\beta\hbar\omega}}{e^{\beta\hbar\omega} + 1}$

Ans. (i) The average energy of a quantum oscillator is given by

$$U = N\left[\tfrac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega - 1}}\right]$$

If we neglect the zero point energy the average energy become

$$U = \frac{N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

Average no. of energy quanta $\frac{U}{N\hbar\omega} = \frac{1}{e^{\beta\hbar\omega} - 1}$

Q. 70. In a particular salt among n-atoms each atom has a spin 1/2 and is associated with a magnetic dipolemoment μ_B. The distance between the magnetic atoms is large enough to make the interaction between them negligible. In otherwords our system is an idealised spin system. The salt is placed in an external magnetic field B. Find the partition function of the individual atom and that for the salt

Ans. $Q_1(V, T) = \sum_r e^{-\beta E_r}$ $E_r = \mu_B B$ for $S = -\frac{1}{2}$ {where μ_B = Bohr magneton}

$= e^{-\beta\mu_B B} + e^{\beta\mu_B B}$, $-\mu_B B$ for $S = \frac{1}{2}$

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Since the salt consist of N number of particles

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$$Q_N(V, T) = \left[Q_1(V,T)\right]^N = \left[e^{-\beta\mu_B B} + e^{\beta\mu_B B}\right]^N \rightarrow \text{distinguishable}$$

Q. 71. Consider a system of two identical particles which may occupy any of the three levels. The lowest energy state $\varepsilon_0 = 0$ is doubly degenerates. The system is in thermal equilibrium at temperature T. Determine the partition function and average energy of the system if particles obey

(i) M-B statistics (ii) B-E statistics (iii) F-D statistics.

Soln: (i) For M-B statistics, $g_i = 16$

$$Q_N(V, T) = \Sigma g_r e^{-\beta E_r} = 4 + 4e^{-\beta\epsilon} + 5e^{-2\beta\epsilon} + 2e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$$

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ell n\, Q_N(V,T) = \frac{\epsilon[4e^{-\beta\epsilon} + 10e^{-2\beta\epsilon} + 6e^{-3\beta\epsilon} + 4e^{-4\beta\epsilon}]}{Q_N(V,T)}$$

(ii) For B-E statistics $Q_N(V, T) = e^{-\beta\epsilon} + e^{-2\beta\epsilon} + e^{-3\beta\epsilon} + e^{-4\beta\epsilon}$

$$\langle E\rangle = \frac{\in[2e^{-\beta\in}+6e^{-2\beta\in}+3e^{-3\beta\in}+4e^{-4\beta\in}]}{Q_N(V,T)}$$

(iii) For F-D statistics:

$$Q_N(V,T) = 1+2e^{-\beta\in}+2e^{-\beta\in}+e^{-3\beta\in}$$

$$\langle E\rangle = \frac{\in(2e^{-\beta\in}+4e^{-2\beta\in}+3e^{-3\beta\in})}{Q_N(V,T)}$$

Problems that appeared in GATE from this section :

G-1. Thermodynamic variables of a system can be volume V, pressure P, temperature T, number of particles N, internal energy E and chemical potential μ, etc. For a system to be specified by Microcanonical (MC), Canonical Ensemble (CE) and Grand Canonical (GC) ensembles, the parameters required for the respective ensembles are

(a) MC : (N, V, T); CE : (E, V, N); GC : (V, T, μ)
(b) MC : (E, V, N); CE : (N, V, T); GC : (V, T, μ)
(c) MC : (V, T, μ); CE : (N, V, T); GC : (E, V, N)
(d) MC : (E, V, N); CE : (V, T, μ); GC : (N, V, T)

[GATE-2008]

Soln. An ensemble is simply a very large collection of identical macroscopic systems which are allowed to interact. There are three most important thermodynamic environment conditions which can represent the interaction of one system with the other. They are—

1. Each system is assumed to be closed and fixed volume but separated from its neighbours by diathermic walls, so that all systems are in thermal equilibrium. i.e., the system is characterized by constants N, V and T. This is a closed isothermal system and called the canonical ensemble. (the particles can exchange energy with each other).
2. Each system is considered to be of constant volume but open and separated from its neighbours by diathermic permeable membrane so that both material and energy can be exchanged between neighbours. This is an open isothermal system characterized by constants μ, V and T where, μ is the chemical potential of each species and is called grand canonical ensemble.
3. Each system is assumed to be concerned with the isolated assembly of independent particles. It is a system of constant volume and is separated from its neighbours with a rigid impermeable adiabatic walls. It can neither exchange energy or material with its neighbours. This is characterized by constants N, V and E and called microcanonical ensemble.

Hence, the correct option is (b).

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G-2. In a classical micro-canonical ensemble for a system of N non-interacting particles, the fundamental volume in phase space which is regarded as "equivalent to one micro-state" is

(a) h^{3N} **(b)** h^{2N} **(c)** h^{N} **(d) h**

where h is the Planck's constant.

[GATE-2002]

Soln. For one particle, $V = dxdp_x = h^3$

For N particle, $V = (h^3)^N = h^{3N}$

Hence correct option is (a).

G-3. Which of the following statements is true?

(a) In a micro-canonical ensemble the total number of particles N and the energy E are constants while in a canonical ensemble N and temperature T are constants.

(b) In a micro-canonical ensemble the total number of particles N is a constant but the energy E is variable while in a canonical ensemble N and T are constants.

(c) In a macro-canonical ensemble N and E are constants while in a canonical ensemble N and T both vary.

(d) In a micro-canonical ensemble N and E are constants while in a canonical ensemble N is a constant but T varies.

[GATE-2002]

Soln. Solution same as solution for G-1.

Hence, the correct answer is (a).

Common Data for Q.G-4 and Q.G-5.

An ensemble of N three-level systems with energies $E = -\epsilon_0, 0, +\epsilon_0$ is in thermal equilibrium at temperature T. Let $\beta = (k_\beta T)^{-1}$

G-4. If $\beta\varepsilon_0 = 2$, the probability of finding the system in the level $\varepsilon = 0$ is:

(a) $(\cos h\, 2)/2$ **(b)** $(\cos h\, 2)^{-1}$ **(c)** $(2\cos h\, 2)^{-1}$ **(d)** $(1+2\cos h\, 2)^{-1}$

[GATE-2004]

Soln. The probability of finding the system in the energy state with energy ε_i may be defined as $P(\varepsilon_i) = \dfrac{e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}}$

But $\varepsilon = 0, -\varepsilon_0, +\varepsilon_0$, hence the probability of finding the system with $\varepsilon = 0$ is

$$P(0) = \frac{e^0}{\left(e^{\beta\varepsilon_0} + e^0 + e^{-\beta\varepsilon_0}\right)}$$

In question $\beta\varepsilon_0 = 2$,

So, $P(0) = \dfrac{e^0}{\left(1 + e^2 + e^{-2}\right)}$ But $\dfrac{e^x + e^{-x}}{2} = \cosh x$

Hence, $P(0) = \dfrac{1}{(1 + 2\cosh x)}$

Hence correct option is (d).

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G-5. The free energy of the system at high temperature $(\text{i.e., } x \equiv \beta\varepsilon_0 << 1)$ is approximately

(a) $-NK_B\, Tx^2$ **(b)** $-NK_B\, T\left[\ln 2 + x^2/2\right]$

(c) $-NK_B T\left[\ln 3 + x^2/3\right]$ **(d)** $-NK_B T \ln 3$

[GATE-2004]

Soln. The Helmholtz free energy of N particles in terms of partition function may be defined as

$F = -Nk_B T\, \ell n\, Z$

where, Z is known as partition function.

Since, $Z = \Sigma e^{-\beta\varepsilon_i} = 1 + e^{-\beta\varepsilon_0} + e^{+\beta\varepsilon_0}$

$= 1 + e^{-x} + e^{+x}$ (where, $x = \beta\varepsilon_0$)

For high temperature $\beta\varepsilon_0 \ll 1 \Rightarrow x \ll 1, \left(\beta = \frac{1}{k_B T}\right)$

Therefore, $e^{-x} \approx (1-x)$ and $e^{+x} \approx (1+x)$ and $Z = 1 + (1-x) + (1+x) = 3$

$\Rightarrow \quad F = -Nk_B T \, \ell n \, 3$

Hence correct option is (d).

THERMODYNAMICAL QUANTITIES IN CANONICAL ENSEMBLE

(Phyisical significance of various statistical quantities in canonical ensemble)

$$P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

where U β can be determined by the eqn.

Internal energy or average energy $U = \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \sum E_r P_r$

$$= -\frac{\partial}{\partial \beta} \ell n \sum_r e^{-\beta E_r}$$

$$= -\frac{\partial}{\partial \beta} \ell n \, Q_N(V,T) \qquad (1)$$

Helmholtz free energy :

$$A = U - TS$$

$$\therefore \quad dA = dU - TdS - SdT$$

$$= TdS - PdV + \mu dN - TdS - SdT \quad \{dQ = TdS = PdV - \mu dN + dU\}$$

$$= -PdV - SdT + \mu dN$$

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Pressure $\boxed{P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}}$ $\boxed{S = -\left(\frac{\partial A}{\partial T}\right)_{V,N}}$ $\boxed{\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}}$

S: entropy; μ: chemical potential

$$\because \quad U = A + TS$$

$$= A - T\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$\boxed{U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right)_{N,V}}$$

$$U = \frac{\partial\left(\frac{A}{T}\right)}{\partial\left(\frac{1}{T}\right)}\Bigg]_{N,V} = \left[\frac{\partial\left(\frac{A}{k_B T}\right)}{\partial\left(\frac{1}{k_B T}\right)}\right]_{N,V}$$

$$\boxed{U = \frac{\partial}{\partial\beta}\left(\frac{A}{k_B T}\right)_{N,V}} \qquad \ldots (2)$$

Comparing eqn (1) and (2)

$$\frac{A}{k_B T} = -\ell n\, Q_N (V,T)$$

$$\boxed{A = -k_B T \ell n\, Q_N (V,T)}$$

A is an extensive (additive) property

Molar specific heat (C_V):

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left[\frac{\partial}{\partial T}(A+TS)\right]_{N,V} = \frac{\partial}{\partial T}\left[A - T\left(\frac{\partial A}{\partial T}\right)_{N,V}\right]$$

$$= \left(\frac{\partial A}{\partial T}\right)_{N,V} - \frac{\partial T}{\partial T}\left(\frac{\partial A}{\partial T}\right)_{N,V} - T\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$\boxed{C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}}$$

Gibb's free Energy :

$$\boxed{G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T}} \qquad \ldots (3)$$

$$A = A\,(N, V, T)$$

$$dA = \left(\frac{\partial A}{\partial N}\right)_{V,T} dN + \left(\frac{\partial A}{\partial V}\right)_{N,T} dV = \mu dN - PdV \qquad (\because \text{since } T = \text{const})$$

Integrating keeping intensive variable constant

$$A = \mu N - PV \qquad \left(\frac{\partial A}{\partial N}\right)_{V,T} = \mu \qquad \left(\frac{\partial A}{\partial V}\right)_{N,T} = -P$$

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Putting this value in above eqn.

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = \left(\frac{\partial A}{\partial N}\right)_{V,T} N + \left(\frac{\partial A}{\partial V}\right)_{N,T} V - V\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

$$= N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu$$

$$\boxed{G = N\mu}$$

Entropy:

$$P_r = Q_N^{-1}\, e^{-\beta E_r}$$

$$\ell n P_r = \ell n\, Q_N^{-1}\, e^{-\beta E_r} = \ell n\, Q_N^{-1} + \ell n\, e^{-\beta E_r} = -\ell n\, Q_N - \beta E_r$$

$$\langle \ell n\, P_r \rangle = -\ell n\, Q_N - \beta \langle E_r \rangle = \frac{A}{k_B T} - \beta U = \beta(A - U) = -\beta TS = -\frac{S}{k_B}$$

$$S = -k_B \langle \ell n\, P_r \rangle$$

$$\boxed{S = -\sum_r P_r \ell n\, P_r} \qquad \ldots (4)$$

If $T = 0$ i.e system is in ground state and we know ground state is unique then

$P_r = 1$ for ground state

$= 0$ for all other state

$$S = -\left(k_B P_0\, \ell n\, P_0 + k_B P_1\, \ell n\, P_1 + \ldots\ldots \ell n\, 1 = 0\right)$$

$= k_B \times 0 = 0$

This is the third law of thermodynamics we also infer that vanishing entropy and perfect statistical order which implies (complete predictability about the system) go together

Largeness of entropy & high degree of statistical disorder (unpredictability) in the system also go together

Eqn (4) also apply in the microcanonical ensemble for each member of system of the ensemble we have a group of Ω state all equally likely to occour. The value of P_r is less than $\frac{1}{\Omega}$ for each of these states and 0 for all other

$$S = -k_B \sum_{r=1}^{\Omega} \left\{ \frac{1}{\Omega} \left(\ell n \frac{1}{\Omega} \right) \right\} = k_B\, \ell n\, \Omega$$

Thermodynamics of classical ideal gas using Canonical Ensemble :

Now we consider an ideal gas consisting of n - molecules (non-interacting), we consider the gas molecule indistinguishable

$$Q_N(V,T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(q,p)}\, d^{3N}q\, d^{3N}p$$

$$Q_1(V,T) = \frac{p^2}{2m}$$

$$\because \quad Q_1(V,T) = \frac{1}{h^3} \int_0^{\infty} e^{-\frac{\beta p^2}{2m}} d^3q\, d^3p$$

$$Q_1(V,T) = \frac{V}{h^3} \int_0^{\infty} e^{-\frac{\beta p^2}{2m}} 4\pi p^2 dp \qquad \left\{ \int d^3q = V \right\}$$

But we know that

$$\int_0^{\infty} e^{-\alpha x^2} x^n dx = \frac{1}{2} \alpha^{-\frac{(n+1)}{2}} \Gamma\left(\frac{n+1}{2}\right)$$

$$\therefore \quad Q_1(V,T) = \frac{V}{h^3} 4\pi \times \frac{1}{2} \left(\frac{\beta}{2m}\right)^{-3/2} \Gamma\left(\frac{3}{2}\right) = \frac{V}{h^3} \times 4\pi \times \frac{1}{2} \left(\frac{2m}{\beta}\right)^{3/2} \frac{1}{2} \sqrt{\pi} \quad \left\{ \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi} \right\}$$

$$\therefore \quad Q_N(V,T) = \frac{V^N}{h^{3N}} (2\pi m k_B T)^{\frac{3N}{2}} \qquad \therefore \quad Q_N(V,T) = \frac{V^N}{h^{3N}} (2\pi m k_B T)^{\frac{3N}{2}}$$

For indistinguishable particle

$$Q_N(V,T) = \frac{V^N}{N!} \left\{ \frac{2\pi m k_B T}{h^2} \right\}^{\frac{3N}{2}} = \frac{V^N}{N! h^{3N}} \left(\sqrt{2\pi m k_B T} \right)^{3N} = \frac{1}{N!} \left[V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right]^N$$

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} - \text{mean thermal wavelength}$$

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$$Q_1(V,T) = \frac{V}{\lambda^3} \text{ for single particle partition function}$$

$$Q_N(V,T) = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$\text{In } Q_N(V,T) = \ell n\left(\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right) = \ell n\left(\frac{V}{\lambda^3}\right)^N - \ell n\, N!$$

$$= N\,\ell n\left(\frac{V}{\lambda^3}\right) - N\log N + N = N\,\ell n\left(\frac{V}{N\lambda^3}\right) + N$$

Helmholtz free Energy (A) :

$$A = -k_B T\,\ell n\, Q_N(V,T)$$

$$= -k_B T\left[N\,\ell n\left(\frac{V}{N\lambda^3}\right) + N\right] = -Nk_B T\left[\ell n\left(\frac{N\lambda^3}{V}\right) - 1\right] = Nk_B T\left[\ell n\frac{N}{V}\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2} - 1\right]$$

Chemical potential :

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \frac{\partial}{\partial T}\left[Nk_B T\left(\ell n\frac{N}{V}\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2} - 1\right)\right]$$

$$= \frac{\partial}{\partial T}\left[Nk_B T\left[\ell n\, N - \ell n\frac{1}{V}\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2} - 1\right]\right]_{T,V} = k_B T\,\ell n\frac{N}{V}\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2}$$

Pressure : $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = -Nk_B T\left(-\frac{1}{V}\right) = \frac{Nk_B T}{V}$

Entropy : $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T}\left[-Nk_B T\,\ell n\left[\frac{N}{V}\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2}\right] + Nk_B T\right]$

$$= Nk_B\,\ell n\left(\frac{N}{V}\right)\left(\frac{h^2}{2\pi mk_B T}\right)^{3/2} + \frac{3}{2}Nk_B + Nk_B = Nk_B\,\ell n\left(\frac{N}{V}\right)\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2} + \frac{5}{2}Nk_B$$

Internal Energy : $U = -\frac{\partial}{\partial\beta}\ell n\left(Q_N(V,T)\right) = -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right) = \frac{3}{2}Nk_B T$

Gibb's free Energy : $G = A + PV = N\mu$

By considering N particles system as independent harmonic oscillator we can solve two important problems 1) The theory of Black body radiation (statistical mechanics of photons) ii) The theory of lattice vibration (statistical mechanics of phonons)

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Case-I: When the oscillators can be treated classically

The hamiltonian is given by

$$H(Q_j p_j) = \frac{P_i^2}{2m} + \frac{1}{2} m\omega^2 q_i^2 \qquad i = 1, 2, 3.....N$$

For the single oscillator the partition function will be

$$Q_1(V,T) = \frac{1}{h}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \exp\left\{-\beta\left(\frac{1}{2}m\omega^2 q^2 + \frac{p^2}{2m}\right)\right\} dpdq$$

$$= \frac{1}{h}\left[\int_{\infty}^{\infty} \exp^{-\beta\left(\frac{1}{2}m\omega^2 q^2\right)} dq + \int_{\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp\right] \qquad \left\{\int_0^{\infty} e^{-\alpha x^2} x^n dx = \frac{1}{2}\alpha^{-\frac{(n+1)}{2}}\Gamma\left(\frac{n+1}{2}\right)\right\}$$

$$= \frac{1}{h}\left(\frac{2\pi}{\beta m\omega^2}\right)^{1/2}\left(\frac{2\pi m}{\beta}\right)^{1/2} = \frac{1}{\beta\hbar\omega} = (\beta\hbar\omega)^{-1}$$

where $h = \frac{h}{2\pi}$. The partition function of the N-oscillator system is given by

$$Q_N(V,T) = [Q_1(V,T)]^N = (\beta\hbar\omega)^{-N}$$

In this case we have assumed the oscillators to be distinguishable (oscillators can be treated as distinguishable if these oscillator representation of energy levels available in the system or they are not particle (even quasiparticle)).

Oscillators can be treated as indistinguishable if we consider these as particle (Photons or Phonons)

Helmholtz free Energy (A) :

$$A = -k_B T \ell n\, Q_N(V,T)$$

$$= -k_B T \ell n (\beta\hbar\omega)^N = Nk_B T \ell n\, \beta\hbar\omega = Nk_B T \ell n \frac{\hbar\omega}{k_B T} \qquad \text{So } A = Nk_B T \ell n \frac{\hbar\omega}{k_B T}$$

Chemical Potential : (μ)

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \frac{\partial}{\partial N} Nk_B T \ell n \frac{\hbar\omega}{k_B T} = k_B T \ell n \frac{\hbar\omega}{k_B T} \qquad \text{So } A = Nk_B T \ell n \frac{\hbar\omega}{k_B T}$$

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Pressure: $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = 0$ because A is independent of V $\qquad$ So $P = 0$

Entropy (s) : $S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T} Nk_B T \ell n \frac{\hbar\omega}{k_B T}$

$$= -\left(\frac{\partial T}{\partial T} \times Nk_B \ell n\, \hbar\omega/k_B T + Nk_B T \times \partial/\partial T \ell n\, \hbar\omega/k_B T\right)$$

$$= -\left(Nk_B \ell n \frac{\hbar\omega}{k_B T} + Nk_B T \times \frac{k_B T}{\hbar\omega} \times \frac{\hbar\omega}{k_B} \times -\frac{1}{T^2}\right)$$

$$= Nk_B \ell n \frac{k_B T}{\hbar\omega} + Nk_B \quad \textbf{or} \quad S = Nk_B\left[\ell n \frac{k_B T}{\hbar\omega} + 1\right]$$

Internal Energy : $U = -\frac{\partial}{\partial\beta}\ \ell n\ Q_N(V,T) = -\frac{\partial}{\partial\beta}\ell n(\beta\hbar\omega)^{-N} = N\frac{\partial}{\partial\beta}\ \ell n\,\beta\hbar\omega$

$$= \frac{1}{\beta\hbar\omega}\times\hbar\omega = \frac{N}{\beta} = Nk_BT \quad \text{So} \quad U = Nk_BT$$

$$\boxed{C_P = C_V = Nk_B}$$

Gibb's free Energy $G = A + PV = A$

Gibb's free Energy = Helmholtz free energy $(P = 0)$

The mean energy per oscillator is in complete agrement with the equipartition theorem i.e. $2\times\frac{1}{2}k_BT$. For we have here two independent quadratic terms in the single oscillator Hamiltonian.

The density of states g(E) of this system from the enpression of partition function we have

$$g(E) = \frac{1}{(\hbar\omega)^N}\frac{1}{2\pi i}\int\frac{e^{\beta E}}{\beta^N}d\beta \qquad (\beta>0)$$

$$g(E) = \begin{cases}\dfrac{1}{(\hbar g\omega)^N}\dfrac{E^{N-1}}{(N-1)!} & \text{for } E \geq 0\\ 0 & \text{for } E \leq 0 \ .....\end{cases}$$

The entropy of the system can be calculate from eqn * by considering $N >> 1$ and using sterling approximation

$$S(N,E) = k_B\,\ell n\,g(E) = k_B\,\ell n\frac{1}{(\hbar\omega)^N}\frac{E^{N-1}}{(N-1)!}$$

For $N >> 1$ $\quad S = k_B\,\ell n\dfrac{1}{(\hbar\omega)^N}\dfrac{E^N}{N!} = k_B\,\ell n\left(\dfrac{E}{\hbar\omega}\right)^N\dfrac{1}{N!}$

$$= k_B\left[N\,\ell n\frac{E}{\hbar\omega} - \ell n\,N!\right] = k_B\left[N\ell n\frac{E}{\hbar\omega} - N\log N + N\right]$$

$$= Nk_B\left[\ell n\frac{E}{N\hbar\omega}+1\right] - (V) \qquad T = \left(\frac{\partial S}{\partial E}\right)_N^{-1} = \frac{E}{N} \quad \text{or} \quad E = Nk_BT$$

Put this value of E in V So we get

$$S = Nk_B\left[\ell n\frac{k_BT}{\hbar\omega}+1\right]$$ which is the entropy we are obtaining by using partition function

Case-II- when the oscillators can be treated quantum mechanically.

Quantum- mechanically the energy eigenvalues of a one dimenstional harmonic oscillator are given by

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega \qquad n = 0, 1, 2.....$$

For single oscillator partition function

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$$Q_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_n e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

$$= e^{\frac{-\beta\hbar\omega}{2}} + e^{\frac{-3\beta\hbar\omega}{2}} + e^{\frac{-5\beta\hbar\omega}{2}} + \ldots\ldots\ldots\ldots$$

$$= e^{\frac{-\beta\hbar\omega}{2}} \left(1 + e^{-\beta\hbar\omega} + e^{-2\hbar\omega} + \ldots\ldots\right.$$

$$= e^{\frac{\frac{-\beta\hbar\omega}{2}}{1-e^{-\beta\hbar\omega}}}$$

$$= \frac{1}{2\left(\frac{e^{\frac{\beta\hbar\omega}{2}} - e^{\frac{-\beta\hbar\omega}{2}}}{2}\right)} = 2\sinh\left(\frac{\beta\hbar\omega}{2}\right)^{-1}$$

$$Q_N(V,T) = \left[Q_1(V,T)\right]^N = \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N}$$

Helmholtz free energy :

$$A = -k_B T \ell n\ Q_N(V,T)$$

$$= -k_B T \ell n \left[2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-N} = Nk_B T \ell n \left[2\sinh\frac{\beta\hbar\omega}{2}\right]$$

$$A = Nk_B T \ell n \left[2\sinh\frac{\hbar\omega}{2k_B T}\right], \quad \text{Where } \beta = \frac{1}{k_B T}$$

Chemical potential (μ):

$$\mu = \frac{\partial A}{\partial N} = k_B T \ell n\, 2\sinh\frac{\hbar\omega}{k_B T} = \frac{A}{N}$$

Pressure: $P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = 0$

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Entropy: (S)

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$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = -\left[\frac{\partial}{\partial T}T \times Nk_B \ell n\, 2\sinh\frac{\hbar\omega}{2k_B T} + T\frac{\partial}{\partial T}Nk_B\left(\ell n\, 2\sinh\frac{\hbar\omega}{2k_B T}\right)\right]$$

$$= -\left[Nk_B \ell n\, 2\sinh\frac{\hbar\omega}{k_B T} + TNk_B \frac{1}{2\sinh\left(\frac{\hbar\omega}{k_B T^2}\right)} \times 2\cos\left(\frac{\hbar\omega}{2k_B T}\right) \times \frac{h\omega}{2k_B} \times \frac{-1}{T^2}\right]$$

$$= -Nk_B \ell n\, 2\sinh\frac{\hbar\omega}{k_B T} + Nk_B \frac{1}{2}\beta\hbar\omega\ \cosh\frac{\beta\hbar\omega}{2}$$

$$= Nk_B\left[\frac{1}{2}\beta\hbar\omega\ \coth\frac{\beta\hbar\omega}{2} - \ell n\left\{2\sinh\left(\frac{\beta\hbar\omega}{2}\right)\right\}\right] = Nk_B \frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1} - \ell n\left(1-e^{-\beta\hbar\omega}\right)$$

Internal Energy :

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right) = -\frac{\partial}{\partial T} Nk_B \ell n\, 2\sinh\frac{\hbar\omega}{2k_BT}$$

$$= -T^2 Nk_B \frac{1}{2\sinh\frac{\hbar\omega}{2k_BT}} \times 2\cosh\frac{\hbar\omega}{2k_BT} \times \frac{\hbar\omega}{2k_B} \times -\frac{1}{T^2}$$

$$= \frac{1}{2} N\hbar\omega \coth\left(\frac{\beta\hbar\omega}{2}\right)$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]$$

Specific Heat: $C_P = C_V = \frac{\partial U}{\partial T} = Nk_B\left(\frac{1}{2}\beta\hbar\omega\right)^2 \text{cosec}^2\text{h}\left(\frac{1}{2}\beta\hbar\omega\right)$

$$= Nk_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{\left(e^{\beta\hbar\omega}-1\right)^2}$$

$$U = N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right)$$

$$\frac{U}{N} = \left(\frac{1}{2}\hbar\omega + k_BT\right) \quad \text{if } \beta\hbar\omega \ll 1$$

Quantum mechanical oscillators does not obey equipartition theorem i.e. mean thermal energy per particle is always greater than k_BT. If $k_BT \ll \hbar\omega$ - Schrodinger oscillator

$k_BT \gg \hbar\omega$ - Plank's oscillator

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In case of classical oscillator mean energy = k_BT but in case of planks oscillator mean energy $k_BT - \frac{1}{2}\hbar\omega$

Q. 72. Show that the partition function $Q_N(V,T)$ of an extreme relativistic gas consisting of N monoatomic molecules with energy momentum relationship $E = pc$ where c = speed of light, is given by

$$Q_N(V,T) = \frac{1}{N!}\left\{8\pi V\left(\frac{RT}{hc}\right)^3\right\}^N$$

Study the thermodynamics of the ... that $PV = \frac{1}{3}U = \frac{V}{2k_BT}$ 4

Q. 73. Consider a system of an extreme relativistic gas consisting of 3N particles moving in 1 dimension. Show that the partition function in this case is given by $\frac{1}{3N!}\left[2L\left(\frac{k_BT}{hc}\right)\right]^{3N}$. L being the length of the space available. Study the thermodynamics and check that weather $PV=\frac{1}{3}U.\frac{U}{N}=3k_BT,\ \gamma=\frac{4}{3}$ or not.

Ans. $$Q_N(V,T)=\left[Q_1(V,T)\right]^N = \frac{1}{N!}\left[\frac{1}{h^3}\int e^{-\beta H}d\omega\right]^N$$

$$= \frac{1}{N!h^{3N}}\int e^{-\beta Pc}d^{3N}p\,d^{3N}q$$

For extreme relativistic case $H = pc$ and $d\omega = d^{3N}\,p\,d^{3N}q$

$$Q_N(V,T)=\frac{V^N}{N!h^{3N}}\left[\int e^{\frac{-pc}{kT}}d^{3N}p\right]^N \quad \left(\int d^{3N}q=\int d^3q_1 d^3q_2 \ldots d^3q_N\right)$$

$$= \frac{V^N}{N!h^{3N}}\left[\int_0^\infty e^{\frac{pc}{kT}}4\pi p^2dp\right]^N$$

$$= \frac{(4\pi V)^N}{N!h^{3N}}\left[\int_0^\infty e^{\frac{pc}{kT}}p^2\,dp\right]^N$$

Let $\frac{pc}{k_BT}=x \quad \Rightarrow \quad \frac{c}{k_BT}dp=dx$

$$\frac{(4\pi V)^N}{N!h^{3N}}\left[\int_0^\infty e^{-x}\left(\frac{k_BTx}{c}\right)^2\frac{k_BT}{c}dx\right] = \frac{(4\pi V)^N}{N!h^{3N}}\left[\left(\frac{k_BT}{c}\right)^3\int_0^\infty e^{-x}x^2dx\right]^N$$

$$\frac{(4\pi V)^N}{N!h^{3N}}\left[\left(\frac{k_BT}{c}\right)^3 2!\right]^N$$

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$$Q_N(V,T) = \frac{1}{N!}\left[8\pi V\left(\frac{k_BT}{hc}\right)^3\right]^N$$

$$\ell n\ Q_N(V,T) = N\,\ell n\,8\pi V\left(\frac{k_BT}{hc}\right)^3 - \log N! = N\,\ell n\,8\pi V\left(\frac{k_BT}{hc}\right)^3 - N\,\ell n\,N + N$$

$$= N\,\ell n\,\frac{8\pi V}{N}\left(\frac{k_BT}{hc}\right)^3 + N$$

$$A=-k_BT\,\ell n\,Q_N(V,T) = -Nk_BT\,\ell n\,\frac{8\pi V}{N}\left(\frac{k_BT}{hc}\right)^3 - Nk_BT$$

$$P = -\left(\frac{\partial A}{\partial V}\right) = Nk_BT \; \frac{\frac{8\pi}{N}\left(\frac{k_BT}{hc}\right)^3}{\frac{8\pi V}{N}\left(\frac{k_BT}{hc}\right)^3} = \frac{Nk_BT}{V}$$

$$\Rightarrow \qquad U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right)$$

$$\text{Now, } U = T^2 \frac{\partial}{\partial T}\left[Nk_B \ell n \frac{8\pi V}{N}\left(\frac{k_BT}{hc}\right)^3 + Nk_B\right]$$

$$= T^2 Nk \times \frac{\frac{8\pi V}{N}\left(\frac{k_B}{hc}\right)^3 3T^2}{\frac{8\pi V}{N}\left(\frac{k_BT}{hc}\right)^3} = \frac{3k_BNT^4}{T^3} = 3Nk_BT$$

$$U = 3Nk_BT$$

Now, $P = \left(\frac{\partial A}{\partial V}\right)_{T,M} = PV = \frac{Nk_BT}{V} \times V = Nk_BT$

and $\frac{1}{3}U = \frac{3Uk_BT}{3} = Nk_BT$

So we get $PV = \frac{1}{3}U$ or $P = \frac{1}{3}\frac{U}{V}$

Now $dQ = dU + PdV$

For adiabic process $dQ = 0$

$dU + PdV = 0 \Rightarrow d(3PV) + PdV = 0$

$3\,PdV + 3\,VdP + PdV = 0$ or $4PdV = -3VdP$

$$\frac{dP}{P} = -\frac{4}{3}\frac{dV}{V}$$

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Integrating $\ell n\, P = -\frac{4}{3}\ell n\, V + c \; - \ell n\; V^{4/3} + c$

$\ell n\, P + \ell n\, V^{4/3} = \text{constant}, \quad PV^{4/3} = \text{constant}$

For this we know $\gamma = \frac{4}{3}$

(2) $Q_N\,(V,T) = \left[Q_1(V,T)\right]^{3N} = \frac{1}{3N!}\left[\frac{1}{h}\int_{\infty}^{\infty} e^{-\beta Pc} dp\, dq\right]^{3N}$

$= \frac{1}{3N!\,h^{3N}} L^{3N}\left[\int e^{-\frac{Pc}{kT}} dp\right]^{3N}$ $\{L \rightarrow \text{Length}\}$

Let $\frac{pc}{k_BT} = x \quad \Rightarrow \quad dp = \frac{k_BT}{c}dx$

$$Q_N(V,T) = \frac{1}{3N!h^{3N}} L^{3N}\left[2\int_0^\infty e^{-x}\frac{k_BT}{c}dx\right]^{3N}$$

$$= \frac{1}{3N!h^{3N}} L^{3N}\left(\frac{k_BT}{c}\right)^{3N}\left[2\int_0^\infty e^{-x}\,dx\right]^{3N}$$

$$= \frac{1}{3N!h^{3N}} L^{3N}\left(\frac{k_BT}{c}\right)^{3N}\left[\left[-2e^{-x}\right]_o^\infty\right]^{3N}$$

$$= \frac{1}{3N!h^{3N}} L^{3N}\left(\frac{k_BT}{c}\right)^{3N} 2^{3N}$$

$$Q_N(V,T) = \frac{1}{3N!}\left[2L\left(\frac{k_BT}{hc}\right)\right]^{3N}$$

THERMODYNAMICS OF MAGNETIC SYSTEM

We consider a system of N dipoles with $I = \frac{1}{2}$, There is no interaction among the dipole. The dipole can be oriented in two direction and the corresponding energies are $E = -\mu_B H \quad \mu_B H = \in$ when placed in magnetic field H.

$$Q_N(V,T) = \left(e^{\beta\in} + e^{-\beta\in}\right)^N = \left[2\cosh(\beta\in)\right]^N$$

Helmholtz free energy :

$$A = -Tk_B \ell n\, Q_N(V,T) = -k_BT \ell n\left[2\cosh(\beta\in)\right]^N$$

$$A = -Nk_BT \ell n\, 2\cosh(\beta\in)$$

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Pressure(P) :

$$P = \left(\frac{\partial A}{\partial V}\right)_{N,T} = 0$$

Entropy (S) :

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk_B \ell n\, 2\cosh\left(\frac{\in}{k_BT}\right) - Nk_BT \times \frac{1}{2\cosh\beta\in} \times \sinh\frac{\in}{k_BT} \times \frac{\in}{k_B} \times \frac{-1}{T^2}$$

$$S = Nk_B\left[\ell n\left\{2\cosh\left(\frac{\in}{k_BT}\right)\right\} - \frac{\in}{k_BT}\tanh\left(\frac{\in}{k_BT}\right)\right]$$

Internal energy (U) :

$$U = -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right) = -N\in\tanh\frac{\in}{k_BT}$$

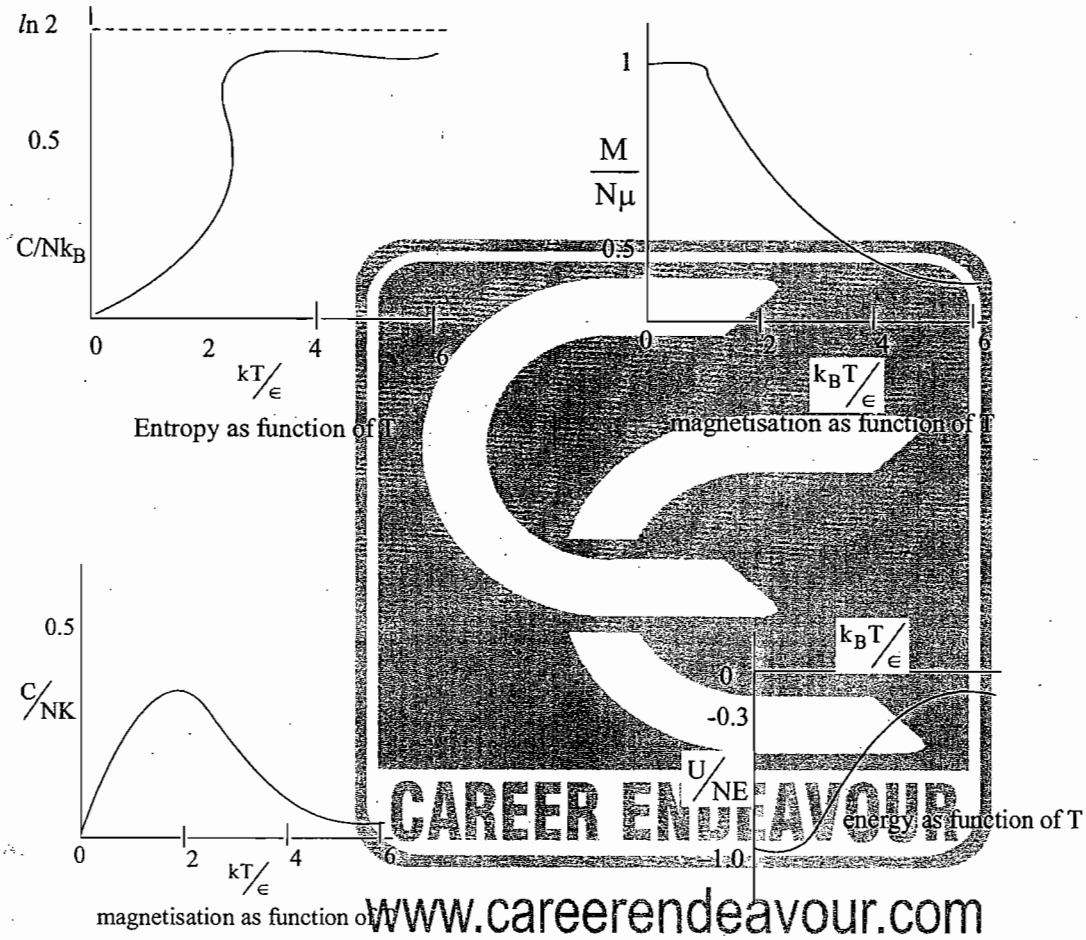
Magnetisation (m) :

$$M = -\left(\frac{\partial A}{\partial H}\right)_T = N\mu_B \tanh \frac{\epsilon}{k_B T}$$

So $U = -M H$

Specific heat

$$C = \left(\frac{\partial U}{\partial T}\right)_H = Nk_B \left(\frac{\epsilon}{k_B T}\right)^2 \sec^2 h\left(\frac{\epsilon}{k_B T}\right)$$



Entropy as function of T

magnetisation as function of T

magnetisation as function of T

energy as function of T

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Energy fluctuations in the canonical ensemble :

$$(\Delta E)^2 = \left(E - \langle E\rangle\right)^2$$

$$\left\langle (\Delta E)^2 \right\rangle = \left\langle \left(E - \langle E\rangle\right)^2 \right\rangle = \left\langle E^2\right\rangle + \langle E\rangle^2 - 2\langle E\rangle^2 = \left\langle E^2\right\rangle - \langle E\rangle^2$$

The average energy $\langle E\rangle = U = \langle E_r\rangle = \dfrac{\sum_r E_r \exp\left(-\beta E_r\right)}{\sum_r \exp\left(-\beta E_r\right) = \sum E_r P_r}$

Now $\dfrac{\partial U}{\partial \beta} = \dfrac{\partial}{\partial \beta}\langle E_r\rangle = \dfrac{\partial}{\partial \beta} \sum \dfrac{E_r \exp\left(-\beta E_r\right)}{\sum \exp\left(-\beta E_r\right)}$

$$= -\frac{\sum_r e^{-\beta E_r}\sum_r E_r^2 e^{-\beta E_r} + \left(\sum_r E_r e^{-\beta E_r}\right)^2}{\left(\sum_r e^{-\beta E_r}\right)^2} = \frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{\left(\sum_r E_r e^{-\beta E_r}\right)^2}{\left(\sum_r e^{-\beta E_r}\right)^2}$$

$$= -\left\langle E_r^2\right\rangle + \left\langle E_r\right\rangle^2 = -\left\langle (\Delta E)^2\right\rangle$$

Now $$\left\langle (\Delta E)^2\right\rangle = \frac{-\partial U}{\partial \beta} = \frac{\partial U}{\partial T}\times\frac{\partial T}{\partial \beta} = k_B T^2 C_V \Rightarrow \sqrt{\left\langle (\Delta E)^2\right\rangle} = \sqrt{kT^2 C_V}$$

Relative root mean square fluctuation in E

$$\frac{\sqrt{k_B T^2 C_V}}{E} = \frac{\text{Of the order of } N^{1/2}}{\text{Of the order of N}} = \text{of the order of } N^{-1/2}$$

N being the no. of particles in the system. Consequently for large N (which is true for every statistical system). The relative root mean square fluctuation in the value of energy is quite negligible. Thus for all practical purpose a system in the canonical ensemble has an energy equal to or almost equal to the mean energy U. The situation in this ensemble is therefore practically the same as in the microcanonical ensembles. That explains why the two ensemble lead to the practically identical results.

Problems that appeared in GATE from this section :

G-1. A paramagnetic system consisting of N spin-half particles, is placed in an external magnetic field. It is found that N/2spins are aligned parallel and the remaining N/2 spins are aligned antiparallel to the magnetic field. The statistical entropy of the system is,

(a) $2Nk_B \ell n\, 2$ **(b)** $\frac{N}{2} k_B \ell n\, 2$ **(c)** $\frac{3N}{2} k_B \ell n\, 2$ **(d)** $Nk_B \ell n\, 2$

[GATE-2012]

Soln. For spin- 1/2 system, number of microstates under equilibrium condition (as the given spin configuration is analogous to equilibrium spin configuration)

$\Omega = (2s+1)^N = 2^N$

$\therefore$ Entropy $S = k_B \ell n\, \Omega = k_B \ell n\, 2^N = Nk_B \ell n\, 2$.

Hence correct option is (d).

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G-2. Consider a linear collection of N independent spin 1/2 particles, each at a fixed location. The entropy of this system is (k_B is the Boltzmann constant)

(a) Zero **(b)** Nk_B **(c)** $\frac{1}{2}Nk_B$ **(d)** $Nk_B\, ln(2)$

[GATE-2013]

Soln. The number of microstates for a particle with spin $S = 2S + 1$.

Therefore, total number of accessible microstates for N independent spins $= (2S+1)^N = \Omega$.

Now, entropy $\equiv k_B \ell n\, \Omega = k_B \ell n \left[(2S+1)^N\right]$

Putting $S = 1/2$

$\Rightarrow$ Entropy $= k_B \ell n \left[(1+1)^N\right] = Nk_B \ell n\, 2$

GRAND CANONICAL ENSEMBLE

Grand canonical ensemble : An ensemble in which system can exchange both energy as well as particles with each other or particle energy reservoir.

Equilibrium : between a system and a particle energy reservoir :

We consider the given system A as immersed in a large reservoir A with which it can exchange both energy as well as particles. After some time both attain the state of mutual equilibrium. In equilibrium both have the same value of T and μ, the no. of particle and energy become variable whose values can lie at any particular time t any where between o to ∞. If at a particular instant of time the system A happens to be in one of its states characterized by the number N_r of particles and the amount E_s of energy then the number of particles in the reservoir who ould be N_r and its energy E_s such that

$$N_r + N_r' = N^{(0)} = \text{constant}$$

$$E_s + E_s' = E^{(0)} = \text{constant}$$

Since the reservoir is supposed to be much larger than the given system

$$\frac{N_r}{N^{(0)}} = \left(1 - \frac{N_r}{N^{(0)}}\right) << 1$$

$$\frac{E_S}{E^{(0)}} = \left(1 - \frac{E_S}{E^{(0)}}\right) << 1$$

The probability P_{rs} that at time t the system A is found to be in an (N_r, E_s) state would be directly proportional to the no. of microstate $\Omega'(N_r', E_s')$ which the reservoir can have for the corresponding macrostate N_r', E_s'

$$P_{rs} \propto \Omega'(N_r', E_s')$$

Or $$P_{rs} = \alpha\, \Omega'\left(N^{(0)} - N_r, E^{(0)} - E_s\right)$$

For simplicity of calculation we take the log

$$\ell n\ P_{rs} = \ell n\, \Omega'\left(N^0 - N_r, E^0 - E_S\right) + \ell n C$$

Now $$\ell n\, \Omega'\left(N^0 - N_r, E^0 - E_S\right) = \ell n\, \Omega'\left(N^0, E_0^0\right) + \left(\frac{\partial\, \ell n\, \Omega'}{\partial N'}\right)_{N'=N^0} (-N_r)$$

$$+ \left(\frac{\partial\, \ell n\, \Omega'}{\partial E'}\right)_{E_S' = E^0} (-E_S) + \ldots..$$

$$\cong \ell n\ \Omega'\left(N^{(0)}, E^{(0)}\right) + \frac{\mu'}{k_B T}(-N_r) - \frac{1}{k_B T} E_S$$

$$\ell n\ P_{rs} \simeq \text{const} - \alpha N_r - \beta E_S \ldots\ldots\ldots\ldots \left\{\alpha = \frac{-\mu}{k_B T},\ \beta = \frac{1}{k_B T}\right\}$$

$$P_{rs} = A e^{-\alpha N_r - \beta E_S}$$

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$$1 = \sum_{rs} P_{rs} = A \sum e^{-\alpha N_r - \beta E_S}$$

$$A = \frac{1}{\sum_{rs} e^{-\alpha N_r - \beta E_S}}, \quad P_r = \frac{e^{-\alpha N_r - \beta E_S}}{\sum_{rs} e^{-\alpha N_r - \beta E_S}}$$

Partition function (Z):

$$Z(z, V, T) = \sum_{rs} e^{-\alpha N_r - \beta E_S}$$

$$Z(\mu, V, T) = \sum_{rs} e^{-\alpha N_r - \beta E_S}$$

$$= \sum_{r} \sum_{s} e^{-\alpha N_r} e^{-\beta E_S} = \sum_{N_r=0}^{\infty} e^{-\alpha N_r} Q_{N_r}(V, T)$$

$$= \sum_{N_r=0}^{\infty} (z)^{N_r} Q_{N_r}(V, T)$$

$Z = e^{-\alpha}$ = fugacity of the system

Q. 74. Consider a system may be either unoccupied or occoupied by one particle with energy 0 and E. Find out 1) partition function of the system 2) Thermal average energy of the system. Thermal average occupancy of the system

Ans.

0	**E**	N_r	E_s
0	0	0	0
1	0	1	0
0	1	1	E

$$Z(\mu, V, T) = \sum_{rs} e^{-\alpha N_r - \beta E_S}$$

$$= e^{-\alpha \times 0 - \beta \times 0} + e^{-\alpha \times 1 - \beta \times 0} + e^{-\alpha \times 1 - \beta \times 1}$$

$$1 + e^{-\alpha} + e^{-\alpha - \beta \epsilon} = 1 + e^{+\frac{\mu}{k_B T}} + e^{\left(\frac{\mu}{k_B T} - \frac{E}{k_B T}\right)}$$

$$U = \langle E_S \rangle = \frac{\sum_{rs} \epsilon_S e^{-\alpha N_r - \beta E_S}}{\sum_{rs} e^{-\alpha N_r - \beta E_S}} = \sum_{rs} E_S \, P_{rs}$$

$$\overline{N} = \langle N_r \rangle = \frac{\sum_{rs} N_r e^{-\alpha N_r - \beta E_S}}{\sum_{rs} e^{-\alpha N_r - \beta E_S}} = \sum_{rs} N_r \, P_{rs}$$

$$\overline{N} = -\frac{\partial}{\partial \alpha} \ell n \, Z(\mu, V, T)_{\beta, V} = e^{-\alpha} - e^{-\alpha - \beta \epsilon} / 1 + e^{-\alpha} + e^{-\alpha - \beta \epsilon}$$

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$$E = -\frac{\partial}{\partial\beta}\ \ell n\, Z(\mu, V, T)_{\alpha,N} = \frac{\in e^{(\mu-\in)\beta}}{1 + e^{\mu\beta} + e^{(\mu-\in)\beta}}$$

Q. 75. Repeat the above problem if each state may be occupied by one particle of the same time

Ans.

	E	N_r	E_s
0	0	0	0
1	o	1	0
0	1	1	E
0	1	2	E

$$Z_N(\mu, V, T) = 1 + e^{-\alpha} + e^{-\alpha-\beta\in} + e^{-2\alpha-\beta\in}$$

Problems that appeared in GATE from this section :

G-1. The partition function of a single gas molecule is Z_α. The partition function of N such non-interacting gas molecules is then given by

(a) $\frac{(Z_\alpha)^N}{N!}$ **(b)** $(Z_\alpha)^N$ **(c)** $N(Z_\alpha)$ **(d)** $\frac{(Z_\alpha)^N}{N}$

[GATE-2007]

Soln. Gas molecules $\Rightarrow$ distinguishable (classical particles). If Z_α = partition function for single particle, then for N distinguishable particles the partition function $= (Z_\alpha)^N$. On the other hand, for N non-distinguishable particles,

the partition function $= \frac{(Z_\alpha)^N}{N!}$

Hence, the correct option is (b).

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PHYSICAL SIGNIFICANCE OF VARIOUS STATISTICAL QUANTITIES

In order to establish a connection between the statistics of the grand canonical ensemble and the thermodynamics of the system we introduce a quantity q defined by

$$q \cong \ell n\, Z(z, V, T) = q(\alpha, \beta, \in_s)$$

$$dq = \frac{\partial q}{\partial\alpha}\, d\alpha + \frac{\partial q}{\partial\beta}\, d\beta + \frac{\partial q}{\partial E_s}\, dE$$

$$Z(z, V, T) = \sum_{r,s} e^{-\alpha N_r - \beta E_S}$$

$$\ell n\ Z(z, V, T) = -\alpha N_r - \beta E_S$$

$$dq = -\bar{N}\, d\alpha - \bar{E}\, d\beta - \frac{\beta}{N}\sum < n_{rs} > dE_s$$

Now we consider an ensemble of N identical system (labelled 1, 2..N mutally sharing a total number of particle $N\bar{N}$ and total energy $N\bar{E}$. Let η_{rs} be the no. of system that have at any time t the number of particle N_r and amount of energy E_s

$$\sum_{r,S} \eta_{rs} = N$$

$$\sum_{r,S} \eta_{r\,S}\, N_r = N\bar{N}$$

$$\sum_{r,S} \eta_{r\,S}\, E_S = N\bar{E}$$

$$q = \ell n\, Z(Z, V, T) = \ell n \left[\sum_{r,S} e^{-\alpha N_r - \beta E_S}\right]$$

$$\frac{\partial q}{\partial \in_S} = \frac{\sum_{r,S} -\beta\ e^{-\alpha N_r - \beta E_S}}{\sum_{r,S} e^{-\alpha N_r - \beta E_S}} = \beta \sum_{r,S} \frac{\langle \eta_{r,s} \rangle}{N}$$

So $$P_{r,s} = \frac{\langle \eta_{r,s} \rangle}{N} = \frac{e^{-\alpha N_r - \beta \in_S}}{\sum_{r,s} e^{-\alpha N_r - \beta \in_s}}$$

Add on both side $\alpha d\bar{N} + \beta d\bar{E}$

$$d\left(q + \bar{N}\alpha + \beta\bar{E}\right) = \alpha d\bar{N} + \beta d\bar{E} - \beta / N \sum_{r,S} \langle \eta_{r,s} \rangle dE_S$$

$$= \beta\left(\frac{\alpha}{\beta} d\bar{N} + d\bar{E} - \frac{1}{N} \sum_{r,s} \langle \eta_{r,s} \rangle dE_S\right)$$

To interprete each term in right hand side bracket we compare this by

$$dQ = d\bar{E} + Pd\bar{V} - \mu d\bar{N}$$

$$dW = \frac{1}{N} \sum \langle \eta_{r,s} \rangle dE_S \qquad d\bar{E} = d\bar{E}$$

So $$\frac{\alpha}{\beta} = -\mu$$

So $$d\left(q + \bar{N}\alpha + \beta\bar{E}\right) = \beta(-\mu d\bar{N} + d\bar{E} + dW) =$$

$$= \beta^{-1}(dQ) = \beta^{-1} TdS$$

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On integrating both side

$$q + \alpha\bar{N} + \beta\bar{E} = \beta TS$$

$$q = \frac{S}{k_B} - \alpha\bar{N} - \beta\bar{E} \qquad \left(\beta TS = \frac{1}{k_B T}.T.S = \frac{S}{k_B}\right)$$

$$= \frac{S}{k_B} + \frac{\mu}{k_B T}\bar{N} - \frac{\bar{E}}{k_B T}$$

$$= \frac{TS + \mu\bar{N} - \bar{E}}{k_B T} = \frac{TS + G - U}{k_B T} \qquad \left(\because \bar{E} = U \quad \mu\bar{N} = G\right)$$

Now $G = A + PV$

So $$q = \frac{TS + A + PV - U}{k_B T} = \frac{PV}{k_B T} \qquad (\because U = A + TS)$$

$$\boxed{q = \frac{PV}{k_B T}}$$

$$\boxed{P = \frac{k_B T}{V} q = \frac{k_B T}{V} \ell n\, Z(Z, V, T)}$$

$$\bar{N} = -\frac{\partial}{\partial \alpha} \ell n\, Z(z, V, T) = -\left(\frac{\partial q}{\partial \alpha}\right)_{V,T}$$

$$U = \bar{E} = -\left(\frac{\partial q}{\partial \beta}\right)_{Z,V} = k_B T^2 \left[\frac{\partial}{\partial T} q(z, V, T)\right]_{Z,V}$$

$$Z = e^{-\alpha} = e^{\mu / k_B T}$$

$$\ell n\, z = \frac{\mu}{k_B T} \Rightarrow \mu = k_B T\, \ell n\, Z$$

$$A = \mu N - PV = N k_B T\, \ell n\, Z - k_B T q$$

$$G = \mu N = N k_B T\, \ell n\, Z$$

$$S = -\left(\frac{\partial A}{\partial T}\right) = -N k_B\, \ell n\, z + k_B q$$

Classical ideal gas : We consider a classical ideal gas consisting of N non-interacting particles

$$Z(z, V, T) = \sum_{N_r=0}^{\infty} z^{N_r}\, Q_{N_r}(V, T)$$

$$Q_{N_r}(V, T) = \left[Q_1(V, T)\right]^{N_r} = \frac{1}{N_r!}\left(\frac{V}{\lambda^3}\right)^{N_r} = \frac{\left[V f(T)\right]^{N_r}}{N_r!}$$

$\left[Q_1(V, T) = \frac{1}{N_r!}\left(\frac{V}{\lambda^3}\right)\right.$ as λ is function of temperature which is diff for difference case (relativistic, non- relativistic). So We write $\left.\lambda^3 = f(T)\right]$

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$$Z(z, V, T) = \sum_{Nr=0}^{\infty} \frac{\{zV f(T)\}^{Nr}}{Nr!}$$

Let $z V f(T) = x$

For diff value N i.e..0, 1, 2.....?

$$= 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + ...$$

$$= \exp\left[zV f(T)\right] \qquad = e^x = e^{[fVf(T)]}$$

$$q = \ell n\, Z(z, V, T) = \ell n \exp\left[z V f(T)\right]$$

$$\boxed{q = zVf(T)}$$

$$P=\frac{k_BT}{V}q(z,V,T)=\frac{k_BT}{V}zVf(T) = z\,k_BTf(T)$$

$$N=z\left(\frac{\partial q}{\partial Z}\right)_{VT}=z\,Vf(T)$$

$$U=k_BT^2\left(\frac{\partial q}{\partial T}\right)=k_BT^2zVf^1(T)$$

$$A=Nk_BT\,\ell n\,Z-zk_BTV\,f(T)$$

$$S=-\left(\frac{\partial A}{\partial T}\right)=-Nk_B\,\ell n\,Z+z\,k_BVf(T)+z\,k_BVf(T)$$

Eliminating z from the expression of P and N we get

$PV=Nk_BT$ (Classical ideal gas)

Eliminating Z from N and U we get

$$U=NkT^2\frac{f'(T)}{f(T)}$$

If $f(T)\ \alpha\ T^n$ then

$$U = Nk_BT^2\times\frac{nT^{n-1}}{T^n}=nNk_BT$$

$$C_V=\frac{\partial U}{\partial T}=nNk_B$$

$$P\,\alpha\frac{U}{V}\Rightarrow P=\frac{1}{n}\frac{U}{V}$$

$n=\frac{3}{2}$ for non-relativistic classical ideal gas

$n=3$ for relativistic classical ideal gas.

Harmonic oscillator :

$Q_1(V,T)=Vf(T)$ for indistinguishable particle

$= f(T)$ for distinguishable particle

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PARTICLE DENSITY AND ENERGY FLUCTUATION IN GRAND CANONICAL ENSEMBLE (CORRESPONDANCE WITH OTHER ENSEMBLE)

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In the grandcanonical ensemble the variable N & E for any member of the ensemble can lie between 0 to ∞. So grandcanonical ensemble appears to be very different from other ensemble (microcanonical and canonical) However the thermodynamical results are same for these three ensemble thus inspite of the strong facial difference, the overall behaviour of a given physical system is practically the same weather it belongs to one kind of ensemble or another. The basic reason for this is that the relative fluctuation in the values of the quantities that vary from member to member in an ensemble are practically negligible. therefore inspite of the different surrounding which different ensemble provide to a given physical system, the overall behaviour of the system is not significantly affected.

Average number of particle

$$\bar{N} = \frac{\sum_{r,S} N_r e^{-\alpha N_r - \beta E_S}}{\sum_{r,S} e^{-\alpha N_r - \beta E_S}}$$

Now $$\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta E_S} = \frac{-\sum_{r,S} e^{-\alpha N_r - \beta E_S} \sum_{r,S} N_r^2 e^{-\alpha N_r - \beta E_S} + \left(\sum_{r,S} N_r e^{-\alpha N_r - \beta E_S}\right)^2}{\left(\sum_{r,S} e^{-\alpha N_r - \beta E_S}\right)^2}$$

$$= -\frac{\sum_{r,s} N_r^2 e^{-\alpha N_r - \beta E_S}}{\sum_{r,s} e^{-\alpha N_r - \beta E_S}} + \frac{\left(\sum_{r,s} N_r e^{-\alpha N_r - \beta E_S}\right)^2}{\sum_{r,s} e^{-\alpha N_r - \beta E_S}}$$

$$= -\langle N_r^2 \rangle + \langle N_r \rangle^2 \quad \ldots (1)$$

But $$(\Delta N)^2 = (N - \langle N \rangle)^2$$

$$\langle (\Delta N)^2 \rangle = \langle N^2 \rangle + \langle N \rangle^2 - 2\langle N \rangle^2 = \langle N^2 \rangle - \langle N \rangle^2 \quad \ldots (2)$$

Comparing (1) and (2)

$$\left(\frac{\partial N}{\partial \alpha}\right)_{\beta, E_s} = -\langle (\Delta N)^2 \rangle$$

$$\langle (\Delta N)^2 \rangle = -\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{\beta, E_S} = -\left(\frac{\partial \bar{N}}{\partial \alpha}\right)_{T, E_S} = -k_B T \left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$$

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As we know $n = \frac{N}{V}$

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So $$\frac{\langle (\Delta n)^2 \rangle}{\bar{n}^2} = \frac{\langle (\Delta N)^2 \rangle}{\bar{N}^2} = \frac{k_B T}{N^2}\left(\frac{\partial \bar{N}}{\partial \mu}\right)_{T,V}$$

$$= \frac{k_B T}{V^2\left(\frac{\bar{N}^2}{V^2}\right)} V \left(\frac{\partial \frac{\bar{N}}{V}}{\partial \mu}\right)_{T,V} = \frac{k_B T}{V^2} U^2 V \left(\frac{\partial\left(\frac{1}{U}\right)}{\partial \mu}\right)_{T,V} \quad \left(\because U = \frac{V}{N}\right)$$

$$\frac{k_B T}{V^2} U^2 V \left(\frac{\partial\left(\frac{1}{U}\right)}{\partial U}\frac{\partial U}{\partial \mu}\right)_{T,V} = \frac{k_B T}{V^2} U^2 V \times -\frac{1}{U^2}\left(\frac{\partial V}{\partial \mu}\right)_{T,V} = -\frac{k_B T}{V}\left(\partial U / \partial \mu\right)_{T,V}$$

$G = A + VP \Rightarrow dG = TdS - PdV - SdT - TdS + PdV + VdP$

$$d\left(\frac{G}{N}\right) = -\frac{S}{N}dT + \frac{V}{N}dP$$

$s \rightarrow$ entropy per particle (specific entropy)

$d\mu = -s\,dT + vdP$

$v \rightarrow$ volume per particle (specific volume)

At Constant temperature $dT = 0 \Rightarrow d\mu = vdP$

So $$\frac{\left\langle(\Delta n)^2\right\rangle}{\bar{n}^2} = -\frac{k_B T}{V}\left(\frac{\partial U}{\partial \mu}\right)_{T,V} = -\frac{k_B T}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right) \qquad (\because d\mu = vdP)$$

$$\frac{\left\langle(\Delta n)^2\right\rangle}{\bar{n}^2} = -\frac{k_B T}{V}\kappa_T$$ where $\kappa_T \rightarrow$ isothermal compressibility

$\approx$ of the order of $\frac{1}{N}$

The relative root mean square fluctuation in the particle density of the given system is of order $N^{-\frac{1}{2}}$. For large values of no. of particle relative root mean square fluctuation in the particle density are negligible. There are exception in the situation like phase transition. In these situation the compressibility of a given system can become excessively large, under these circumstances the isothermal compressibility can very well be of the order of N, the relative root mean square fluctuation in particle density n can then be 0 (1). Thus in the region of phase transition, especially at the critical points, large flauctation in particle density exist and account for phenomena like critical opalescence. Under these circumstance the formalism of grand canonical ensemble leads to the result that are not identical which the ones following from the corresponding canonical ensemble. It is clear that in such cases the formalism of grand canonical ensemble have to be preferred because only this one will provide a correct picture of the actual physical situation.

Fluctuation in energy : ?

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DIATOMIC MOLECULE

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If there are N atoms in a molecule and are rigidly bound together, then there must be 3N degree of freedom out of these 3 corresponding to translational motion of the molecule as a whole and 3 or less than 3 corresponds to rotational a whole vibrational mode for non-linear polyatomic (3N–6)

Vibrational mode for linear polyatomic (3N–5)

Translational, D.O.F + Rotational D.O.F. + Vibrational D.O.F = 3N

Thermodynamic Properties of a diatomic molecule :

If change in energy $(\Delta E) < k_B T$ between two successive level then energy level variation can be treated as continous and classical description is applicable. If $\Delta E < k_B T$ then energy variation can be treated as discontinous and quantum description is applicable.

If a molecule has Translational, Rotational & Vibrational motion then the partition function of the molecule can be written as

$$Z = Z_t Z_R Z_V \quad \text{or} \quad Q = Q_t\, Q_R\, Q_V$$

Now consider a gas of N diatomic non-interacting molecules.

Tanslational partition function :

$$Z_t = \frac{V}{h^3}(2\pi m k_B T)^{3/2} = \frac{V}{\lambda^3}$$

For a gas of N diatomic molecule

$$Z_t = \left(\frac{(z_{1t})^N}{N!}\right)$$

$$\ell n\, Z_t = \ell n\left[\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N\right] = \ell n\left(\frac{V}{\lambda^3}\right)^N - \ell n\, N!$$

$$= N\,\ell n\frac{V}{\lambda^3} - N\,\ell nN + N = N\,\ell n\left(\frac{V}{N\lambda^3}\right) + N$$

Helmholtz free energy :

$$A = -k_B T\,\ell n\, Z_t = -k_B T\left[N\,\ell n\left(\frac{V}{N\lambda^3}\right) + N\right]$$

$$= N T k_B\left[\ell n\left(\frac{N\lambda^3}{V}\right) - 1\right] = N k_B T\left[\ell n\frac{N}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^{3/2} - 1\right]$$

Internal energy :

$$U = -\frac{\partial}{\partial P}\ell n\, Z_t \quad \text{or} \quad -T^2\frac{\partial}{\partial T}\left(\frac{A}{T}\right) = \frac{3}{2}Nk_B T$$

Specific heat :

$$C = \frac{\partial}{\partial T}\quad U = \frac{3}{2}Nk_B$$

Rotational partition function :

$$Z = \sum_r g_r e^{-\beta E_r} \qquad \text{But} \quad E_r = \frac{h^2}{8\pi^2 I}J(J+1)$$

$$Z_{1r} = \sum_J (2J+1)e^{-\beta E_r}$$

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Where I = moment of inertia, J = rotational quantum number.

The summation can't be change into intergration for small value of I and T but for large value of I and T the energy separation between the level is small and we can change summation into integration and we can calculate the approximate value of rotational partition function.

$$Z_{1r} = \int_o^\infty 2J\, e^{-\frac{h^2J^2}{8\pi^2 I k_B T}}\, dJ \qquad \int_o^\infty 2J\, e^{\frac{h^2J^2}{8\pi^2 I k_B T}}\, dJ$$

$$Z_{1r} = \frac{8\pi^2 I k_B T}{h^2} \qquad \text{Put } \alpha = \frac{h^2}{8\pi^2 I k T},\ t = J^2$$

$$dt = 2JdJ$$

$$Z_r = (Z_{1r})^N = \left(\frac{8\pi^2 I k_B T}{h^2}\right)^N$$

$$Z_r = \left(\frac{8\pi^2 I k_B T}{h^2}\right)^N$$

$$\left[\int_0^\infty e^{-\alpha t}dt = \frac{e^{-\alpha t}}{-\alpha}\right]_0^\infty = \frac{-1}{\alpha}\left[e^{-\alpha t}\right]_0^\infty = \frac{-1}{\alpha}(0-1) = \frac{1}{\alpha}$$

Helmholtz free energy (A) :

$$A = -k_B T \ell n\, Z_r = -k_B T \ell n \left(\frac{8\pi^2 I k_B T}{h^2}\right)^N = -N k_B T \ell n \frac{8\pi^2 I k_B T}{h^2}$$

Internal energy (U) :

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right) = -T^2 \frac{\partial}{\partial T} - N k_B \ell n \frac{8\pi^2 I k_B T}{h^2}$$

$$T^2 \times N k_B \times \frac{h^2}{8\pi^2 I k_B T} \times \frac{8\pi^2 I k_B}{h^2} = N k_B T$$

$$U = \langle E \rangle = N k_B T = 2 \times \frac{1}{2} N k_B T$$

Vibrational partition function :

$$Z_{1V} = \sum g_r\, e^{-\beta E_r}$$

$g_r = 1$ for one dimensional harmonic oscillator

$$= \sum e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}$$

$$= e^{\frac{\frac{-\beta\hbar\omega}{2}}{1-e^{-\beta\hbar\omega}}}$$

$$A = -\ell n\, Z_{1r} = \ell n \left(\frac{e^{\frac{-\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}\right) = \frac{\beta\hbar\omega}{2} + \beta\hbar\omega$$

$$= \frac{\beta\hbar\omega}{2} = \frac{\hbar\omega}{2k_B T}$$

$$U = \langle E \rangle = \frac{1}{2} N\hbar\omega + \frac{N\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}-1}}$$

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Classical Oscillator:

For each degree of freedom mean thermal energy for translational motion $\frac{1}{2}k_B T$ for rotational motion $\frac{1}{2}k_B T$ and for vibrational motion $k_B T$.

Nuclear spin effect in diatomic molecule:

Partition function for hetronuclear diatomic molecule

$$Z_r = (2S+1)(2S'+1)\,\frac{8\pi^2 I k_B T}{h^2}$$

Partition function for homonuclear diatomic molecule

$$Z_r = (2S+1)^2 \times \frac{1}{2} \frac{8\pi^2 I k_B T}{h^2} = (2S+1)^2 \frac{4\pi^2 I k_B T}{h^2}$$

In a homonuclear diatomic molecule the two atoms will be of same kind. They have same spin. The spin of two same atom may be either parallel or antiparallel. If spins are parallel then resultant spin one(1) (ortho) and for antiparallel spin resultan (Spin Zero (para))

Now in general if the spin of each nuclei is I. The resultant spin of the diatomic molecule will be either 2I for parallel arrangement or zero for antiparallel arrangement. The possible value are 2I, $2I-2$, ...2, 1, 0

$$S = 2I - n \qquad n = 0, 1, 2$$

$$\frac{\text{Statistical weight factor for ortho}}{\text{Statistical weight factor for para}} = \frac{\sum_n 2(2I-n)+1 \qquad n = 0, 2, 4}{\sum_n 2(2I-n)+1 \qquad n = 1, 3, 5.}$$

$$= \frac{4I+1+4I-3+4I-7.....3}{4I-1+4I-5+4I-9.....1}$$

$$= \frac{\frac{(2I+1)}{4}(4I+1+3)}{\frac{(2I+1)}{4}(4I-1+1)} = \frac{(2I+1)(I+1)}{I(2I+1)}$$

Z_r = Statistical weight factor $\times \sum_J (2j+1)\, e^{-\frac{J(J+1)h^2}{8\pi^2 I k_B T}}$

$$= (2i+1)(i+1) \sum_{J=1,3,5} (2J+1)\, e^{-\frac{\beta J(J+1)h^2}{8\pi^2 I k_B T}} + i(2i+1) \sum_{J=0,2,4} (2j+1)\, e^{-\frac{\beta J(J+1)h^2}{8\pi^2 I k_B T}}$$

$$= (2i+1)(i+1) + i(2i+1) \frac{8\pi^2 I k_B T}{2h^2}$$

$$\boxed{Z_r = (2i+1)^2 \frac{4\pi^2 I k_B T}{h^2}}$$

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AVERAGE THERMAL ENERGY FOR A LINEAR POLYATOMIC MOLECULE

,T and

$$F = \underbrace{\frac{3}{2}k_B T}_{\text{Translational}} + 2 \times \underbrace{\frac{1}{2}k_B T}_{\text{Rotational}} + \underbrace{(3N-5)k_B T}_{\text{Vibrational}}$$

$$= (6N-5)\frac{k_B T}{2} \rightarrow \text{for linear polyatomic molecule}$$

$$= \frac{3}{2}k_B T + 3 \times \frac{1}{2}k_B T + (3N-6)k_B T$$

$= (6N-6)\frac{k_B T}{2}$ for non linear polyatomic molecule.

Specific heat:

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = (6N-6)\frac{k_B}{2}$$

Q. 76. In a system in thermal equilibrium at absolute temperature T, two states with energy difference 4.83×10^{-21} J occour with relative probability e^2. Deduce the temperature ($k_B = 1.38 \times 10^{-23}$ J/K)

Ans. $\Delta E = 4.83\times10^{-23}$

$$\frac{P_1}{P_2} = e^2$$

$$P_i = Ce^{-\beta E_i}$$

$$P_1 = Ce^{-\beta E_1} \qquad P_2 = Ce^{-\beta E_2}$$

$$\frac{P_1}{P_2} = \frac{Ce^{-\beta E_1}}{Ce^{-\beta E_2}} = e^{-\beta(E_1-E_2)} = e^{-\beta(E_2-E_1)}$$

$$e^2 = e^{(E_2-E_1)}$$

$$2 = \beta(E_2 - E_1)$$

$$2 = \frac{1}{k_B T}(E_2 - E_1)$$

$$2k_B T = E_2 - E_1 \Rightarrow T = \frac{E_2 - E_1}{2k_B}$$

$$= \frac{4.83\times10^{-23}\,J}{2\times1.38\times10^{-23}\,J/K} = 1.75\,K$$

Q. 77. A diatomic gas in thermal equilibrium have temperature 500K. Its rotational constant $2.0cm^{-1}$. Calculate the relative populations in the rotational states.

Ans.

Population $E = \frac{h^2}{8\pi^2 I}J(J+1) \qquad B = \frac{h}{8\pi^2 IC}$

$$N_J = \frac{N(2J+1)e^{-\beta E_J}}{\sum_J e^{-\beta E_J}}$$

But $BhC = 3.96\times10^{-16}$ erg.

$$\frac{N_{10}}{N_0} = 91.28 \quad \text{Ans.}$$

$$\frac{N_{20}}{N_0} = 3.371 \text{ Ans}$$

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Equipartition theorem or law of Equipartition of Energy :

When a system obeying classical statistical mechanics is in thermal equilibrium with a heat bath at temperature T. The mean contribution of each quadratic term to the total energy (mean thermal energy) is $\frac{1}{2}k_BT$.

OR

The total kinetic energy of a dynamical system consisting of a large number of particle in thermal equilibrium is equally divided among its all degrees of freedom and average energy associated with each degree of freedom is $\frac{1}{2}k_BT$. If the degree of freedom is f, the average energy is $\frac{1}{2}fk_BT$.

Proof : Let us take a system, the classical description of which requires f position co-ordinates $(q_1, q_2, q_3 \ldots\ldots q_f)$ and corresponding moment $p_1\ p_2\ p_3 \ldots p_f$ The energy of the system is a function of these co-ordinates.

$$U = \epsilon_i(p_i) + U'(p_1\ p_2 \ldots\ p_f, q_1\ q_2 \ldots q_f)$$

Prime indicates that that part doesn't contain P_i

$$\bar{\epsilon}_i = \frac{\int \epsilon_i\ e^{-\beta U} dq_1\, dq_2 \ldots\ dq_f\ dp,\ dp_2 \ldots\ dp_f}{\int e^{-\beta U}\, dq_1\, dq_2 \ldots\ dq_f\, dp_1\, dp_2 \ldots dp_f}$$

$$= \frac{\int \epsilon_i\, e^{-\beta(\epsilon_i + U')} dq_1\, dq_2 \ldots dq_f\, dp_i\, dp_2 \ldots dp_f}{\int e^{-\beta(\epsilon_i + U')} dq_1\, d_2 \ldots dq_f\, dp_i\, dp_2 \ldots dp_f}$$

$$= \frac{\int \epsilon_i\, e^{-\beta\epsilon_i} dp_i \int e^{-\beta U'} dq_1\, dq_2 \ldots dq_f\, dp_1\, dp_2 \ldots dp_f}{\int e^{-\beta\epsilon_i} dp_i \int e^{-\beta U'} dq_1\, dq_2 \ldots dq_f\, dp_1\, dp_2 \ldots dp_f}$$

$$\epsilon_i = \frac{p_i^2}{2m}$$

$$\frac{\int \frac{p_i^2}{2m} e^{-\frac{\beta p_i^2}{2m}} dp_i}{\int e^{-\frac{\beta p_i^2}{2m}} dp_i}$$

According to equipartition theorem the average energy of free particle at temperature T should be $\frac{3}{2}k_BT$.

The average kinetic energy of the centre of mass motion of a polyatomic molecule should be $\frac{3}{2}k_BT$.

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Limitation :

(1) The law of equipartition of energy is applicable only so long as the system can be described classically.

(2) This is applicable above room temp but at very low temperature where the gas is about to liquify it is not true. Higher the temperature of the sytem better the validity of the theorem.

Problems that appeared in GATE from this section :

G-1. A system of N non-interacting classical point particles constrained to move on the two-dimensional surface of a sphere. The internal energy of the system is

(a) $\frac{3}{2}Nk_BT$ **(b)** $\frac{1}{2}Nk_BT$ **(c)** Nk_BT **(d)** $\frac{5}{2}Nk_BT$

[GATE-2010]

Soln. Since, particle is moving on two-dimensional surface its degree of freedom = 2
Hence, for N non-interacting particle total degree of freedom = 2N
The energy per degree of freedom = $1/2\, k_BT$

Hence, total energy $U = 2N \times \frac{1}{2}k_BT$

$\Rightarrow U = Nk_BT$

Hence, the correct option is (c).

G-2. Consider a system of two non-interacting classical particles which can occupy any of the three energy levels with energy values $E = 0, \varepsilon$ and 2ε having degeneracies $g(E) = 1, 2$ and 4 respectively. The mean energy of the system is

(a) $\varepsilon\left[\frac{4\exp\left(\frac{-\varepsilon}{k_BT}\right)+8\exp\left(\frac{-2\varepsilon}{k_BT}\right)}{1+2\exp\left(\frac{-\varepsilon}{k_BT}\right)+4\exp\left(\frac{-2\varepsilon}{k_BT}\right)}\right]$ **(b)** $\varepsilon\left[\frac{2\exp\left(\frac{-\varepsilon}{k_BT}\right)+8\exp\left(\frac{-2\varepsilon}{k_BT}\right)}{1+2\exp\left(\frac{\varepsilon}{k_BT}\right)+4\exp\left(\frac{-2\varepsilon}{k_BT}\right)}\right]$

(c) $\varepsilon\left[\frac{2\exp\left(\frac{-\varepsilon}{k_BT}\right)+4\exp\left(\frac{-2\varepsilon}{k_BT}\right)}{1+2\exp\left(\frac{-\varepsilon}{k_BT}\right)+4\exp\left(\frac{2\varepsilon}{k_BT}\right)}\right]$ **(d)** $\varepsilon\left[\frac{\exp\left(\frac{-\varepsilon}{k_BT}\right)+2\exp\left(\frac{-2\varepsilon}{k_BT}\right)}{1+\exp\left(\frac{-\varepsilon}{k_BT}\right)+\exp\left(\frac{-2\varepsilon}{k_BT}\right)}\right]$

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[GATE-2008]

Soln. Total energy due to a particular level = occupancy of the level × energy.

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$\therefore\ E_1 = 0 \cdot \exp\left[-\frac{0}{k_BT}\right]$

$E_2 = \varepsilon \cdot g(E) \cdot \exp\left[-\frac{\varepsilon}{k_BT}\right] = 2\varepsilon \exp\left[-\frac{\varepsilon}{k_BT}\right]$

Similarly, $E_3 = 2\varepsilon \cdot 4\exp\left[-\frac{2\varepsilon}{k_BT}\right]$

Also, mean energy $= \frac{\sum_i E_i}{\text{total occupancy}} = \frac{E_1 + E_2 + E_3}{\sum_i g_i \exp\left(-\frac{\varepsilon_i}{k_BT}\right)}$

$$= \frac{0 + 2\varepsilon \exp\left(-\frac{\varepsilon}{k_B T}\right) + 8\varepsilon \exp\left(-\frac{2\varepsilon}{k_B T}\right)}{\exp\left(-\frac{0}{k_B T}\right) + 2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)} = \varepsilon\left[\frac{2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)}{1 + 2\exp\left(-\frac{\varepsilon}{k_B T}\right) + 4\exp\left(-\frac{2\varepsilon}{k_B T}\right)}\right]$$

Hence correct option is (b).

G-3. A system has two energy levels with energies ε and 2ε. The lower level is 4-fold degenerate while the upper level is doubly degenerate. If there are N non-interacting classical particles in the system, which is in thermodynamic equilibrium at a temperature T, the fraction of particles in the upper level is:

(a) $\frac{1}{1+e^{-\varepsilon/k_B T}}$ **(b)** $\frac{1}{1+2e^{\varepsilon/k_B T}}$ **(c)** $\frac{1}{2e^{\varepsilon/k_B T}+4e^{2\varepsilon/k_B T}}$ **(d)** $\frac{1}{2e^{\varepsilon/k_B T}-4e^{2\varepsilon/k_B T}}$

[GATE-2011]

Soln. $E_L = E,\ E_U = 2E$

$g_L = 4,\ g_U = 2$

$$N(E_i) \propto g_i \exp\left[-\frac{E_i}{k_B T}\right]$$

$$\therefore\ N(E_L) = C \times g_L \exp\left[-\frac{E_L}{k_B T}\right]$$

Similarly, $N(E_U) = C \times g_U \exp\left[-\frac{E_U}{k_B T}\right]$

The fraction of particles in upper level $= \frac{N(E_U)}{N(E_U) + N(E_L)}$

$$= \frac{2 \cdot \exp\left[-\frac{2E}{k_B T}\right]}{4\exp\left[-\frac{E}{k_B T}\right] + 2\exp\left[-\frac{2E}{k_B T}\right]} = \frac{1}{1 + 2\exp\left[-\frac{E}{k_B T}\right]}$$

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Hence correct option is (b).

G-4. The mean internal of a one-dimensional classical harmonic oscillator in equilibrium with a heat bath of temperature T is:

(a) $\frac{1}{2}k_B T$ **(b)** $k_B T$ **(c)** $\frac{3}{2}k_B T$ **(d)** $3k_B T$

[GATE-2006]

Soln. Since, the one-dimensional classical harmonic oscillator has two degrees of freedom and according to the law of equipartition of energy each degree of freedom has $1/2\ k_B T$ energy, where k_B is Boltzmann constant and T is temperature. Hence, total mean energy of one-dimensional classical harmonic oscillator is $k_B T$.
Hence correct option is (b).

G-5. **If the partition function of a harmonic oscillator with frequency ω at a temperature T is $\frac{k_B T}{\hbar\omega}$, then the free energy of N such independent oscillators is:**

(a) $\frac{3}{2}Nk_BT$ **(b)** $k_BT\ln\frac{\hbar\omega}{k_BT}$ **(c)** $Nk_BT\ln\frac{\hbar\omega}{k_BT}$ **(d)** $Nk_BT\ln\frac{\hbar\omega}{2k_BT}$

[GATE-2005]

Soln. The Helmholtz' free energy of N independent harmonic oscillator in terms of partition function Z is

$$F = -Nk_BT\ \ell n\ Z$$

In question, $Z = \frac{k_BT}{\hbar\omega}$

So, $F = -Nk_BT\ \ell n\ Z = Nk_BT\ \ell n\frac{1}{Z} = Nk_BT\ \ell n\frac{\hbar\omega}{k_BT}$

Hence correct option is (c).

Statement for Linked Answer Question G-6 and G-7
An ensemble of quantum harmonic oscillator is kept at a finite temperature $T = 1/k_B\beta$.

G-6. **The partition function of a single oscillator with energy levels $\left(n+\frac{1}{2}\right)\hbar\omega$ is given by**

(a) $Z = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$ **(b)** $Z = \frac{e^{-\beta\hbar\omega/2}}{1+e^{-\beta\hbar\omega}}$ **(c)** $Z = \frac{1}{1-e^{-\beta\hbar\omega}}$ **(d)** $Z = \frac{1}{1+e^{-\beta\hbar\omega}}$

[GATE-2007]

Soln. $Z = \sum_i e^{-\beta\varepsilon_i}$ where, $\varepsilon_i = \left[(i-1)+\frac{1}{2}\right]\hbar\omega \quad (i = 1, 2, 3, \ldots)$

$$\therefore\ Z = e^{-\beta\hbar\omega/2} + e^{-3\beta\hbar\omega/2} + e^{-5\beta\hbar\omega/2} + \ldots = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

Hence correct option is (a).

G-7. **The average number of energy quanta of the oscillators is given by**

(a) $\langle n\rangle = \frac{1}{e^{\beta\hbar\omega}-1}$ **(b)** $\langle n\rangle = \frac{e^{\beta\hbar\omega}}{e^{\beta\hbar\omega}-1}$ **(c)** $\langle n\rangle = \frac{1}{e^{\beta\hbar\omega}+1}$ **(d)** $\langle n\rangle = \frac{e^{-\beta\hbar\omega}}{e^{\beta\hbar\omega}+1}$

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[GATE-2007]

Soln. $\langle n\rangle = \frac{\sum n_i e^{-\beta\varepsilon_i}}{Z} \qquad (n_i = 0, 1, 2, 3, \ldots.)$

$$= \frac{0\cdot e^{-\beta\hbar\omega/2} + 1\cdot e^{-3\beta\hbar\omega/2} + 2\cdot e^{-5\beta\hbar\omega/2} + \ldots.}{Z} = \frac{1\cdot e^{-3\beta\hbar\omega/2} + 2\cdot e^{-5\beta\hbar\omega/2} + 3\cdot e^{-7\beta\hbar\omega/2} + \ldots.}{e^{-\beta\hbar\omega/2}/(1-e^{-\beta\hbar\omega})}$$

$$= \frac{\left(1\cdot e^{-3\beta\hbar\omega/2} + 2\cdot e^{-5\beta\hbar\omega/2} + 3\cdot e^{-7\beta\hbar\omega/2} + \ldots.\right)\left(1-e^{-\beta\hbar\omega}\right)}{e^{-\beta\hbar\omega/2}} = \left(e^{-\beta\hbar\omega} + 2e^{-2\beta\hbar\omega} + 3e^{-3\beta\hbar\omega} + \ldots.\right)\left(1-e^{-\beta\hbar\omega}\right)$$

$$= \left[e^{-\beta\hbar\omega} + 2e^{-2\beta\hbar\omega} + 3e^{-3\beta\hbar\omega} + \ldots.\right] - \left[e^{-2\beta\hbar\omega} + 2e^{-3\beta\hbar\omega} + 3e^{-4\beta\hbar\omega} + \ldots.\right]$$

$$= e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + e^{-3\beta\hbar\omega} + \ldots.$$

$$= \frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega}-1}$$

G-8. **A classical gas of molecules, each of mass m, is in thermal equilibrium at the absolute temperature T. The velocity components of the molecules along the Cartesian axes are v_x, v_y and v_z. The mean value of $(v_x + v_y)^2$ is**

(a) $\frac{k_B T}{m}$ **(b)** $\frac{3k_B T}{2m}$ **(c)** $\frac{1}{2}\frac{k_B T}{m}$ **(d)** $\frac{2k_B T}{m}$

[GATE-2012]

Soln. $\langle (v_x + v_y)^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + 2\langle v_x v_y \rangle$

Putting $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{k_B T}{m}$ $\left(\because \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{3}{2}k_B T\right)$

and $\langle v_x v_y \rangle = 0$, $\langle (v_x + v_y)^2 \rangle = \frac{k_B T}{m} + \frac{k_B T}{m} + 0 = \frac{2k_B T}{m}$

Hence correct option is (d).

G-9. **Consider a system whose three energy levels are given by 0, ε and 2ε. The energy level ε is two-fold degenerate and the other two are non-degenerate. The partition function of the system with** $\beta = \frac{1}{k_B T}$ **is given by**

(a) $1 + 2e^{-\beta\epsilon}$ **(b)** $2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$ **(c)** $\left(1 + e^{-\beta\epsilon}\right)^2$ **(d)** $1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$

[GATE-2012]

Soln. For the given energy levels the partition function can be written as

$z = e^{-\beta \cdot 0} + 2e^{-\beta\varepsilon} + e^{-\beta \cdot 2\varepsilon}$; where the factor 2 is due to two fold degeneracy of energy level ε.

Therefore, $z = 1 + 2e^{-\beta\varepsilon} + (e^{-\beta\varepsilon})^2 = (1 + e^{-\beta\varepsilon})^2$

Hence correct option is (c).

G-10. **At a certain temperature T, the average speed of nitrogen molecules in air is found to be 400 m/s. The most probable and the root mean square speeds of the molecules are, respectively,**

(a) 355 m/s, 434 m/s **(b) 820 m/s, 917 m/s**

(c) 152 m/s, 301 m/s **(d) 422 m/s, 600 m/s**

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[GATE-2012]

Soln. Given, $C_{av} = 400$ m/s

Now, $C_{av} = \sqrt{\frac{8k_B T}{\pi m}}$ and $C_{mp} = \sqrt{\frac{2k_B T}{m}} \Rightarrow \frac{C_{av}}{C_{mp}} = \frac{2}{\sqrt{\pi}}$

$C_{mp} = \frac{\sqrt{\pi}}{2} C_{av} = \frac{\sqrt{\pi}}{2} \times 400 = \sqrt{\pi} \times 200 \approx 355$ m/s

Now, $C_{\text{rms}} = \sqrt{\frac{3k_B T}{m}}$

$\Rightarrow \frac{C_{av}}{C_{\text{rms}}} = \sqrt{\frac{8}{3\pi}} \Rightarrow C_{\text{rms}} = \sqrt{\frac{3\pi}{8}} \times 400 \approx 434$ m/s

Hence correct option is (a).

G-11. At a given temperature, T, the average energy per particle of a non-interacting gas of two-dimensional classical harmoic oscillator is _____ k_BT.

[GATE-2014]

Soln. According to two-dimensional harmonic oscillator, we consider the vibration of molecules in two dimensions. Vibrational mode in one dimension provides k_BT energy. In two dimension, total energy is vibrational molecules.

Hence, 2 is correct answer $= 2 \times (k_BT)$ energy.

G-12. For a black body radiation in a cavity, photons are created and annihilated freely as a result of emission and absorption by the walls of the cavity. This is because [GATE-2015]

(a) the chemical potential of the photons is zero

(b) photons obey Pauli exclusion principle

(c) photons are spin-1 particles

(d) the entropy of the photons is very large

Soln. Since, photon has zero chemical potential, the number of photons cannot be conserved. Thus, photons can be created and annihilated.

Hence correct option is (a).

G-13. The entropy of a gas containing N particles enclosed in a volume V is given by $S = Nk_B \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right)$, where E is the total energy, a is a constant and k_B is the Boltzmann constant. The chemical potential μ of the system at a temperature T is given by

(a) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{5}{2}\right]$ **(b)** $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{3}{2}\right]$

(c) $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{5}{2}\right]$ **(d)** $\mu = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{3/2}}\right) - \frac{3}{2}\right]$

[GATE-2015]

Soln. $\mu = -T\left(\frac{\partial S}{\partial N}\right) = -Tk_B \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - Tk_BN \cdot \frac{N^{5/2}}{aVE^{3/2}} \cdot \frac{aVE^{3/2}}{N^{7/2}}\left(-\frac{5}{2}\right)$

$= -Tk_B \ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) + \frac{5}{2}k_BT = -k_BT\left[\ell n\left(\frac{aVE^{3/2}}{N^{5/2}}\right) - \frac{5}{2}\right]$

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Hence correct option is (a).

Common Data for Q. G-14 and Q. G-15:

There are four energy levels E, $2E$, $3E$ and $4E$ (where $E > 0$). The canonical partition function of two particles is, if these particles are

G-14. Two identical fermions

(a) $e^{-2\beta E} + e^{-4\beta E} + e^{-6\beta E} + e^{-8\beta E}$ **(b)** $e^{-3\beta E} + e^{-4\beta E} + 2e^{-5\beta E} + e^{-6\beta E} + e^{-7\beta E}$

(c) $(e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E})^2$ **(d)** $e^{-2\beta E} - e^{-4\beta E} + e^{-6\beta E} - e^{-8\beta E}$

[GATE-2013]

Soln. For fermions the distribution of particles can be as illustrated below.

Energy Level → / Configuration ↓	E	$2E$	$3E$	$4E$
I	A	A		
II	A		A	
III	A			A
IV		A	A	
V		A		A
VI			A	A

From the above table it is clear that :-
Number of configuration with total energy $3E = 1$.
Number of configuration with total energy $4E = 1$.
Number of configuration with total energy $5E = 2$.
Number of configuration with total energy $6E = 1$.
Number of configuration with total energy $7E = 1$.
Hence correct option is (b).

G-15. Two distinguishable particles

(a) $e^{-2\beta E} + e^{-4\beta E} + e^{-6\beta E} + e^{-8\beta E}$ **(b)** $e^{-3\beta E} + e^{-4\beta E} + 2e^{-5\beta E} + e^{-6\beta E} + e^{-7\beta E}$

(c) $(e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E})^2$ **(d)** $e^{-2\beta E} - e^{-4\beta E} + e^{-6\beta E} - e^{-8\beta E}$

[GATE-2013]

Soln. Since the particles are indistinguishable they can be treated classically i.e., any number of particles can be present in any level.
Now, the partition function for one particle with the given energy levels can be written as
$Z = e^{-\beta E} + e^{-2\beta E} + e^{-3\beta E} + e^{-4\beta E}$
Therefore, the partition function for two particles equal to Z^2
Hence correct option is (c).

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Chapter 7

Distribution laws of classical & quantum statistical physics

THE BOUNDARY BETWEEN CLASSICAL & QUANTUM REGIME

Mean thermal wavelength or mean thermal de-Broglie wavelength.

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \hbar\left(\frac{2\pi\beta}{m}\right)^{1/2}$$

Degeneracy discriminant factor:

$$n\lambda^3 = \frac{N}{V}\frac{h^3}{(2\pi m k_B T)^{3/2}}$$

(i) If $n\lambda^3 << 1$ for classical consideration or non-degenerate case

$$\lambda << \left(\frac{V}{N}\right)^{1/3} \rightarrow \text{Mean equilibrium separation}$$

(ii) If $n\lambda^3$ is small but non equal to zero departure for classical behaviour sets in

(iii) If $n\lambda^3 \simeq 1$ for quantum consideration

(iv) If $n\lambda^3 >> 1$ degenerate

(v) If $n\lambda^3 \rightarrow \infty$ highly or complete degenerate.

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Distribution laws :

Statistics

Classical

System of distinguishable identical particle of any spin (maxwell) Boltzmann statistics
Ex: Classical ideal gas

Quantum

(1) Apply to the system of indistinguishable identical particle.

Bose-Einstein

Apply to indistinguishable zero or integral spin particle
Ex: Photon, Phonon, He_4, π meson

Femi-Dirac

Apply to ½ odd integral spin indistinguishable identical particle
Ex: Electron, neutron, He_3, p-meson neutrino.

Now we consider a system of two particle A & B and each particle can be in any one of the state 1, 2, 3. The

7

Particle state	M – B			B – E			F – D		
Microstate	1	2	3	1	2	3	1	2	3
	A	B			A	A		A	A
	B	A			A	A			A A
		A	B A			A	A	A	
	B		A AA						
	B		A			AA			
	AB					AA			
			AB						
Total number of State			9			6			3

$$f = \frac{\text{Probability that the two particles are found in same state}}{\text{Probability that the particles are found in diff. particle state}}$$

$$f_{M-B} = \frac{3/9}{6/9} = \frac{1}{2} \qquad f_{B-E} = \frac{3/6}{3/6} = 1$$

$$f_{FD} = \frac{0/3}{3/3} = 0$$

Now we consider a system of N identical particles. Let these particles be divided into group such that $n_1, n_2 \ldots n_i$ particles lies in the group having energy $\epsilon_1\ \epsilon_2 \ldots \epsilon_i$ respectively But g_i be the statistical weight of the ith group (shell)

$$\sum n_i = N$$

$$\sum \epsilon_i\, n_i = E \text{ (Total energy)}$$

Problems that appeared in GATE from this section :

G-1. It is necessary to apply quantum statistics to a system of particles, if

(a) there is substantial overlap between the wave functions of the particles

(b) the mean free path of the particles is comparable to the inter-particle separation

(c) the particles have identical mass and charge

(d) the particles are interacting

[GATE-2007]

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Soln. The quantum realm begins when de Broglie wavelength of the particles (or associated with the particles) becomes comparable to the size of the particle. Under this condition, the wavelength of the particles starts overlapping.

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Hence, the correct option is (a).

G-2. The wavefunctions of two identical particles in stated n and s are given by $\phi_n(r_1)$ & $\phi_s(r_2)$, respectively. The particles obey Maxwell-Boltzmann statistics. The state of the combined two particles system is expressed as

(a) $\phi_n(r_1) + \phi_s(r_2)$

(b) $\frac{1}{\sqrt{2}}[\phi_n(r_1)\,\phi_s(r_2) + \phi_n(r_2)\,\phi_s(r_1)]$

(c) $\frac{1}{\sqrt{2}}[\phi_n(r_1)\,\phi_s(r_2) - \phi_n(r_2)\,\phi_s(r_1)]$

(d) $\phi_n(r_1)\,\phi_s(r_2)$

[GATE-2006]

Soln. According to quantum mechanical theory of identical particles:

For two particles in states n and s represented by wave functions $\phi_n(r_1)$ & $\phi_s(r_2)$ respectively,

We have $\psi(r_1, r_2)$ ≡ wave function representing the combined state of the two particles.

3. The

Case I. Distinguishable particles (Maxwell-Boltzmann statistics)

$$\psi_{ns}(r_1, r_2) \equiv \phi_n(r_1)\,\phi_s(r_2)$$

Case II. Indistinguishable particles

Case II (A) Fermions (Fermi-dirac statistics)

$$\psi_{ns}(r_1, r_2) \equiv \frac{1}{\sqrt{2}}\left[\phi_n(r_1)\,\phi_s(r_2) - \phi_n(r_2)\,\phi_s(r_1)\right]$$

Case II (B) Bosons (Bose-Einstein statistics)

$$\psi_{ns}(r_1, r_2) \equiv \frac{1}{\sqrt{2}}\left[\phi_n(r_1)\,\phi_s(r_2) + \phi_n(r_2)\,\phi_s(r_1)\right]$$

Hence, the correct option is (d).

G-3. The total number of accessible states of N non-interacting particles of spin 1/2 is

(a) 2^N **(b) N^2** **(c) $2^{N/2}$** **(d) N**

[GATE-2005]

Soln. The total number of accessible states for N spin 1/2 particles = 2^N. But how many of them can be occupied depends on energy of the particles.

Hence, the correct option is (a).

Common Data for Questions G-4 and G-5:

Consider a two levels quantum system with energies $\varepsilon_1 = 0, \varepsilon_2 = \varepsilon$.

G-4. The Helmholtz free energy of the system is given by

(a) $-k_B T\, \ell n\,(1 + e^{-\varepsilon/k_B T})$ **(b)** $k_B T\, \ell n\,(1 + e^{-\varepsilon/k_B T})$

(c) $\frac{3}{2} k_B T$ **(d)** $\varepsilon - k_B T$

[GATE-2009]

Soln. $F = -k_B T \log\left[e^{-\varepsilon_1/k_B T} + e^{-\varepsilon_2/k_B T}\right]$

$\because\ \varepsilon_1 = 0,\ \varepsilon_2 = \varepsilon$

$F = -k_B T \log\left[1 + e^{-\varepsilon/k_B T}\right]$

Hence correct option is (a).

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G-5. The specific heat of the system is given by

(a) $\frac{\varepsilon}{k_B T} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$ **(b)** $\frac{\varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$

(c) $-\frac{\varepsilon^2\, e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$ **(d)** $\frac{\varepsilon^2}{k_B T^2} \cdot \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})^2}$

[GATE-2009]

Soln. $\frac{\partial F}{\partial T} = \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})} \times \left(\frac{-\varepsilon}{k_B T^2}\right) \times (-k_B T) = \frac{\varepsilon}{T} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$

$$C_V = \frac{\varepsilon}{k_B T} \times \frac{\partial F}{\partial T} = \frac{\varepsilon^2}{k_B T^2} \frac{e^{-\varepsilon/k_B T}}{(1 + e^{-\varepsilon/k_B T})}$$

Hence correct option is (b).

G-6. Two particles are said to be distinguishable when
(a) the average distance between them is large compared to their de Broglie wavelength.
(b) the average distance between them is small compared to their de Broglie wavelengths.
(c) they have overlapping wavepackets.
(d) their total wave function is symmetric under particle exchange.

[GATE-2001]

Soln. Distinguishable means they can be described classically (No need of quantum mechanics).
Hence correct option is (a).

G-7. A monatomic crystalline solid comprises of N atoms, out of which n atoms are in interstitial positions. If the available interstitial sites are N, then number of possible microstates is:

(a) $\frac{(N'+n)!}{n!N!}$ **(b)** $\frac{(N+n)!}{n!(N'-n)!}\frac{(N'+n)!}{n!(N'-n)!}$ **(c)** $\frac{N!}{n!(N'-n)!}$ **(d)** $\frac{N!}{n!(N-n)!}\frac{N'!}{n!(N'-n)!}$

2005] upied

[GATE-2006]

Soln. According to probability theory,

Number of ways for choosing n atoms out of N atoms $= {}^{N}C_n = \frac{N!}{n!(N-n)!}$ and number of ways for putting n atoms in N' site $= {}^{N'}C_n = \frac{N'!}{n!(N'-n)!}$

$\therefore$ Total number of microstates are, $\Omega = \frac{N'!}{n!(N'-n)!} \times \frac{N!}{n!(N-n)!}$

Hence correct option is (d).

2009] **G-8. Two identical particles have to be distributed among three energy levels. let r_B, r_F and r_C represent the ratios of probability of finding two particles to that of finding one particle in a given enegy state. The subscripts B, E and C correspond to whether the particles are bosons, fermions and classical particles, respectively. The $r_B : r_F : r_C$ is equal to**

(a) $\frac{1}{2}:0:1$ **(b)** $1:\frac{1}{2}:1$ **(c)** $1:\frac{1}{2}:\frac{1}{2}$ **(d)** $1:0:\frac{1}{2}$

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[GATE-2008]

Soln. Boson follow Bose-Einstein statistics (BE), fermions follow Fermi-Dirac statistics (FD), classical particles follow Maxwell-Boltzmann statistics (MB).
The distribution of 2 particles is shown in the following table.
For identical particles (BE and FD) $\Rightarrow$ A, A (2 similar particles)
For distinguishable particles and (MB) $\Rightarrow$ A, B (2 different particles)

2009]

Statistics ⟶	M-B				B-E				F-D		
Particle-states ⟶	1	2	3		1	2	3		1	2	3
Various Micro-states possible	A	B			A	A			A	A	
	B	A				A	A			A	A
		A	B		A		A		A		A
		B	A		AA						
	B		A			AA					
	A		B				AA				
	AB										
		AB									
			AB								
Total number of system-states	9				6				3		

$$r_F = \frac{0}{3/3} = 0, \quad r_C = \frac{3/9}{6/9} = \frac{1}{2}, \quad r_B = \frac{3/6}{3/6} = 1$$

Hence correct option is (d).

G-9. Which of the following relations between the particle number density n and temperature T must hold good for a gas consisting of non-interacting particles to be described by quantum statistics?

(a) $n/T^{1/2} \ll 1$ **(b)** $n/T^{3/2} \ll 1$

(c) $n/T^{3/2} \gg 1$ **(d)** $n/T^{1/2}$ and $n/T^{3/2}$ can have any value.

[GATE-2002]

Soln. For quantum consideration, the mean interparticle distance between the particles must be comparable to the de Broglie wavelength of the particles.

Now, n = number density of the particles.

$$\therefore \left(\frac{1}{n}\right)^{1/3} \cong \text{mean inter-particle distance} \qquad ...(i)$$

Also, $\lambda = \frac{h}{p}$ (de Broglie wavelength) $= \frac{h}{\sqrt{2mE}} = \frac{h}{\sqrt{2mk_BT}}$ ...(ii)

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The given condition for quantum consideration can be satisfied using (i) and (ii) if $\left(\frac{1}{n}\right)^{1/3} \simeq \lambda$

$$\Rightarrow \lambda(n)^{1/3} \simeq 1 \Rightarrow \lambda^3 n \simeq 1 \Rightarrow \frac{h^3}{(2mk_BT)^{3/2}} n \simeq 1 \Rightarrow \frac{h^3}{(2mk_B)^{3/2}} \cdot \frac{n}{T^{3/2}} \simeq 1$$

$$\Rightarrow \frac{n}{T^{3/2}} \simeq \frac{(2mk_B)^{3/2}}{h^3} \simeq 10^{27} \qquad \text{(for sub-atomic particles)}$$

$$\Rightarrow \frac{n}{T^{3/2}} \gg 1$$

Hence correct option is (c).

Common Data for Questions G-10 and G-11:
A gas of N particles is enclosed in a volume V at a temperature T. The logarithm of the partition function is given by $\ln Z = N\ln\left[(V-bN)(k_BT)^{3/2}\right]$ where b is a constant with appropriate dimensions.

G-10. If P is the pressure of the gas, the equation of state is given by

(a) $P(V-bN) = Nk_BT$ **(b)** $P(V-bN) = k_BT$

(c) $P(V-b) = Nk_BT$ **(d)** $P(V-b) = Nk_BT$

[GATE-2003]

Soln. $P = T\left(\frac{\partial S}{\partial V}\right)_U$

$$S = k_B\left[\frac{\partial}{\partial T}(T\ \ell n\ Z)\right] = k_B\frac{\partial}{\partial T}\left[TN\ \ell n\left[\frac{(V-bN)}{(k_BT)^{3/2}}\right]\right] = k_B\frac{\partial}{\partial T}\left\{TN\ \ell n\,(V-bN) - \frac{TN^3}{2}\ell n\,k_BT\right\}$$

$$= k_BN\ \ell n\,(V-bN) - k_B\left[\frac{3}{2}N\ell n\,k_BT + \frac{3}{2}TN\cdot\frac{1}{k_BT}\cdot k_B\right]$$

$$S = k_BN\ \ell n\,(V-bN) - \frac{3}{2}k_BN\ \ell n\,k_BT - \frac{3}{2}N$$

Now, $P = T\left(\frac{\partial S}{\partial V}\right) = T\left\{\frac{k_BN}{(V-bN)}\right\}$

$\Rightarrow\ P(V-bN) = Nk_BT$

Hence correct option is (a).

G-11. The internal energy of the gas is given by

(a) $U = (1/2)k_BT$ **(b)** $U = (1/2)k_BT$ **(c)** $U = (3/2)Nk_BT$ **(d)** $U = 2Nk_BT$

[GATE-2003]

Soln. $U = -\frac{\partial\ \ell n\ Z}{\partial\beta} = -N\frac{\beta^{3/2}}{(V-bN)}\cdot\frac{3}{2}\beta^{-5/2} = (-N)\left(\frac{3}{2}\right)\beta^{3/2-5/2} = \frac{3}{2}N\beta^{-1} = \frac{3}{2}Nk_BT$

$\Rightarrow\ U = \frac{3}{2}Nk_BT$

Hence correct option is (c).

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G-12. For a system of two bosons, each of which can occupy any of the two energy levels 0 and ε, the mean energy of the system at a temperature T with $\beta = \frac{1}{k_BT}$ is given by

(a) $\frac{\varepsilon\ e^{-\beta\varepsilon} + 2\varepsilon\ e^{-2\beta\varepsilon}}{1+2e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$ **(b)** $\frac{1}{2e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$ **(c)** $\frac{2\varepsilon\ e^{-\beta\varepsilon} + \varepsilon\ e^{-2\beta\varepsilon}}{2+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$ **(d)** $\frac{\varepsilon\ e^{-\beta\varepsilon} + 2\varepsilon\ e^{-2\beta\varepsilon}}{2+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$

[GATE-2014]

Soln. Mean energy for a system is defined as $\bar{\varepsilon} = \frac{\sum\varepsilon_i e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}}$

Now, $\varepsilon_i = 0$, ε and $\beta = \frac{1}{k_B T}$

Now, two Bosons can be distributed in following 4 ways.

ε ———	ε A ———	ε A A ———	ε A ———
0 A A ———	0 A ———	0 ———	0 A ———
I	II	III	IV

Looking all the above four configurations,

$\bar{\varepsilon}$ can be written as

$$\bar{\varepsilon} = \frac{0 \cdot e^{-\beta \cdot 0} + \varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-2\beta\varepsilon}}{e^{-\beta \cdot 0} + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}} = \frac{\varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-2\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

Hence correct option is (a).

G-13. Consider a system of 3 fermions, which can occupy any of the 4 available energy states with equal probability. The entropy of the system is **[GATE-2014]**

(a) $k_B \ln 2$ **(b)** $2k_B \ln 2$ **(c)** $2k_B \ln 2$ **(d)** $3k_B \ln 4$

Soln. The distribution of 3 fermions (A, A, A) in 4 energy states (I, II, III, IV) is illustrated in the following table :-

States → / Microstates ↓	1	2	3	4
I	A	A	A	
II	A	A		A
III	A		A	A
IV		A	A	A
Total no. of microstates = 4				

Now, entropy is defined as $S = k_B \ell n \Omega$

where Ω = number of accessible microstates (which is = 4 in present case).

Therefore, $S = k_B \ell n 4 = k_B \ell n 2^2 = 2k_B \ell n 2$.

Hence correct option is (b).

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G-14. Consider a system of N non-interacting spin-$\frac{1}{2}$ particles, each having a magnetic moment μ, is in a magnetic field $\vec{B} = B\hat{z}$. If E is the total energy of the system, the number of accessible microstates Ω is given by

(a) $\Omega = \dfrac{N!}{\frac{1}{2}\left(N - \frac{E}{\mu B}\right)! \, \frac{1}{2}\left(N + \frac{E}{\mu B}\right)!}$ **(b)** $\Omega = \dfrac{\left(N - \frac{E}{\mu B}\right)!}{\left(N + \frac{E}{\mu B}\right)!}$

(c) $\Omega = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)! \, \frac{1}{2}\left(N + \frac{E}{\mu B}\right)!$ **(d)** $\Omega = \dfrac{N!}{\left(N + \frac{E}{\mu B}\right)!}$ **[GATE-2015]**

Soln. Suppose out of N non-interacting spin- 1/2 particles, n have magnetic moment $+\mu$ and $N-n$ particles have magnetic moment $-\mu$.

Then, total energy $E = n\mu B - (N-n)\mu B$

$$\Rightarrow \quad E = 2n\mu B - N\mu B$$

$$\Rightarrow \quad n = \frac{1}{2}\left(N + \frac{E}{\mu B}\right) \qquad \text{...(i)}$$

Therefore, $N - n = \frac{1}{2}\left(N - \frac{E}{\mu B}\right)$ ...(ii)

Now, number of ways in which n particles out of total N particles can be selected to have magnetic moment $+\mu$ is given by ${}^{N}C_{n}$.

Therefore, $\Omega = {}^{N}C_{n} = \frac{N!}{n!(N-n)!}$ ...(iii)

$$\Rightarrow \quad \Omega = \frac{N!}{\frac{1}{2}\left[N + \frac{E}{\mu B}\right]!\,\frac{1}{2}\left[N - \frac{E}{\mu B}\right]!} \quad \text{(Substituting (i) and (ii) in (iii))}$$

Hence correct option is (c).

G-15. The average energy U of a one dimensional quantum oscillator of frequency ω and in contact with a heat bath at temperature T is given by

(a) $U = \frac{1}{2}\hbar\omega \coth\left(\frac{1}{2}\beta\hbar\omega\right)$ **(b)** $U = \frac{1}{2}\hbar\omega \sinh\left(\frac{1}{2}\beta\hbar\omega\right)$

(c) $U = \frac{1}{2}\hbar\omega \tanh\left(\frac{1}{2}\beta\hbar\omega\right)$ **(d)** $U = \frac{1}{2}\hbar\omega \cosh\left(\frac{1}{2}\beta\hbar\omega\right)$

[GATE-2015]

Soln. The energy of a linear harmonic oscillator is given by

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega \qquad \text{...(i)}$$

where, $n = 0, 1, 2, \ldots$. Therefore, the partition function $Z(T)$ of the oscillator is

$$Z(T) = \sum_n e^{-\beta\varepsilon_n} = \exp\left[-\beta(\hbar\omega/2)\right] + \exp\left[-\beta(3\hbar\omega/2)\right] + \ldots.$$

$$= e^{-\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + \ldots.) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \text{ as } e^{-\hbar\omega\beta} < 1$$

$$\text{or} \quad \ell n\, Z = -\frac{1}{2}\beta\hbar\omega - \ell n(1 - e^{-\beta\hbar\omega}) \qquad \text{...(ii)}$$

Using equation $\bar{U} = -\frac{\partial\, \ell n\, Z}{\partial\beta}$, the average energy becomes

$$\bar{U} = -\frac{\partial\, \ell n\, Z}{\partial\beta} = \frac{1}{2}\hbar\omega + \frac{-e^{-\beta\hbar\omega} \times -\hbar\omega}{1 - e^{-\beta\hbar\omega}} \text{ or } \bar{U} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} \qquad \text{...(iii)}$$

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$$\Rightarrow \bar{U} = \frac{\hbar\omega}{2}\left[1 + \frac{2}{e^{\beta\hbar\omega}-1}\right] = \frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega}-1+2}{e^{\beta\hbar\omega}-1}\right] = \frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega}+1}{e^{\beta\hbar\omega}-1}\right]$$

$$= \frac{\hbar\omega}{2}\left[\frac{e^{\beta\hbar\omega/2}\left(e^{\beta\hbar\omega/2}+e^{-\beta\hbar\omega/2}\right)}{e^{\beta\hbar\omega/2}\left(e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}\right)}\right] = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)$$

Hence correct option is (a).

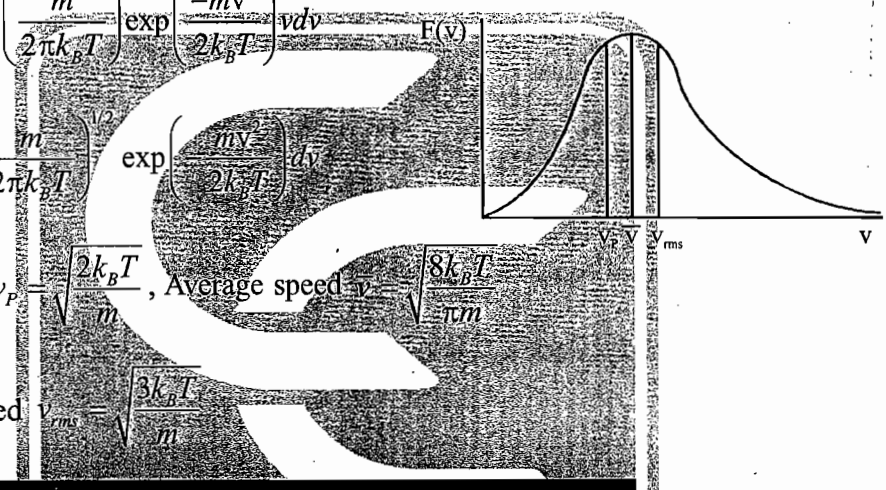
Maxwell's Velocity Distribution Law

The number of molecules having velocity in range v to v + dv in three dimension. If their are N number of particles in the system then

For 3D $f(v)dv = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2}\exp\left(\frac{-mv^2}{2k_B T}\right)v^2 dv$

For 2D $f(v)dv = 2\pi N\left(\frac{m}{2\pi k_B T}\right)\exp\left(\frac{-mv^2}{2k_B T}\right)vdv$

For 1D $f(v)dv = N\left(\frac{m}{2\pi k_B T}\right)^{1/2}\exp\left(\frac{-mv^2}{2k_B T}\right)dv$



Most probable speed $v_P = \sqrt{\frac{2k_B T}{m}}$, Average speed $\bar{v} = \sqrt{\frac{8k_B T}{\pi m}}$

Root mean square speed $v_{rms} = \sqrt{\frac{3k_B T}{m}}$

Problems that appeared in GATE from this section :

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G-1. Hydrogen molecules (mass m) are in thermal equilibrium at a temperature T. Assuming classical distribution of velocity, the most probable speed at room temperature is:

(a) $(k_B T)/m$ **(b)** $2k_B T/m$

(c) $\left(\sqrt{2k_B T/m}\right)$ **(d)** $mn/\left(\sqrt{2}k_B T\right)$

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[GATE-2003]

Soln. The probability that molecule will posses a speed v is $P(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_B T)}$. For the most probable speed, the probability of the speed must be maximum. Therefore, we differentiate the above equation with respect to v for equating it to zero i.e., $\frac{dP(v)}{dv}$

$$= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\left[2ve^{-mv^2/2k_B T} - \frac{v^3 m}{k_B T}\times e^{-mv^2/2k_B T}\right] = 0$$

$$\Rightarrow 2v\,e^{-mv^2/2k_B T} = \frac{v^3 m}{k_B T}\,e^{-mv^2/2k_B T} \Rightarrow v^2 = \frac{2k_B T}{m} \text{ or } v_{mp} = \sqrt{\frac{2k_B T}{m}}$$

G-2. **Consider a gas of atoms obeying Maxwell-Boltzmann statistics. The average value of $e^{\vec{a}\cdot\vec{p}}$ over all the momenta $\vec{p}$ of each of the particles (where $\vec{a}$ is a constant vector and a is its magnitude, m is the mass of each atom. T is temperature and k is Boltzmann's constant) is**

(a) one **(b)** zero **(c)** $e^{-\frac{1}{2}a^2 mk_BT}$ **(d)** $e^{-\frac{3}{2}a^2 mk_BT}$

[GATE-2013]

Soln. $\left\langle e^{\vec{a}\cdot\vec{p}}\right\rangle = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f\left(p_x, p_y, p_z\right) e^{\vec{a}\cdot\vec{p}}\, dp_x\, dp_y\, dp_z$ where $f\left(p_x, p_y, p_z\right)$ is Maxwell momentum distribution function.

$$\left\langle e^{\vec{a}\cdot\vec{p}}\right\rangle = \int_{-\infty}^{\infty} A_x e^{-\frac{p_x^2}{2mk_BT}} e^{a_x p_x} dp_x \int_{-\infty}^{\infty} A_y e^{-\frac{p_y^2}{2mk_BT}} e^{a_y p_y} dp_y \int_{-\infty}^{\infty} A_z e^{-\frac{p_z^2}{2mk_BT}} e^{a_z p_z} dp_z$$

$$\Rightarrow \left\langle e^{\vec{a}\cdot\vec{p}}\right\rangle = e^{-\frac{(a_x^2+a_y^2+a_z^2)mk_BT}{2}} \int_{-\infty}^{\infty} A_x e^{-\frac{(p_x - mk_BTa_x)^2}{2mk_BT}} \int_{-\infty}^{\infty} A_y e^{-\frac{(p_y - mk_BTa_y)^2}{2mk_BT}} \int_{-\infty}^{\infty} A_z e^{-\frac{(p_z - mk_BTa_z)^2}{2mk_BT}}$$

$$\Rightarrow \left\langle e^{\vec{a}\cdot\vec{p}}\right\rangle = e^{-\frac{(a_x^2+a_y^2+a_z^2)mk_BT}{2}} e^{a^2 mk_BT}$$

Hence correct option is (c).

Maxwell - Boltzmann : The number of distinct ways (microstate) associated with ith cell in M.B.S

$$(\omega)_{M-B}(i) = \left(g_i\right)^{n_i}$$

$$W_{M-B}(i) = N!\prod_i \frac{\left(g_i\right)^{n_i}}{n_i!} \rightarrow \text{distinguishable} \quad \ldots (1)$$

$$= \prod_i \frac{\left(g_i\right)^{n_i}}{n_i!} \rightarrow \text{indistinguishable} \quad \ldots (2)$$

Bose- Einstein: $\omega_{BE} = \dfrac{\left(n_i + g_i - 1\right)!}{n_i!\left(g_i - 1\right)!}$

$$\omega_{BE} = \frac{\left(n_i + g_i - 1\right)!}{n_i!\left(g_i - 1\right)!} \quad \ldots (3)$$

Femi-Dirac: $\omega_{FD}(i) = \dfrac{g_i!}{n_i\left(g_i - n_i\right)!}$

$$\omega_{FD}(i) = \prod_i \frac{g_i!}{n_i\left(g_i - n_i\right)!} \quad \ldots (4)$$

To determine most proable distribution function we use Lagrangian undetermined multiplier method.

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Bose Einstein distribution function :

$$\sum n_i = N \Rightarrow \sum \delta n_i = 0$$

$$\sum \in_i n_i = E \Rightarrow \sum \in_i \delta n_i = 0$$

$$W = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}$$

$$\ell n\ \omega = \sum_i \ell n\,(n_i + g_i - 1)! - \ell n\, n_i! - \ell n\ (g_i - 1)!$$

$$= \sum_i \ell n\,(n_i + g_i)! - \ell n\ n_i! - \ell n\, g_i!$$

$$= \sum_i (n_i + g_i)\ell n\,(n_i + g_i) - (n_i + g_i) - n\ell n\, n + n - g_i\, \ell n\, g_i + g_i$$

$$\ell n\ \omega = = \sum_i (n_i + g_i)\ell n\,(n_i + g_i) - n_i \ell n\, n_i - g_i\ \ell n\, g_i$$

$$\delta\, \ell n\, \omega = \sum_i (n_i + g_i)\frac{1}{n_i + g_i}\delta n_i + \delta n_i\ \ell n\,(n_i + g_i) - n_i \times \frac{\delta n_i}{n_i} - \delta n_i n\, n_i$$

$$= \sum_i\ \ell n\ \frac{n_i + g_i}{n_i}\delta n_i$$

By using the Lagrange undetermined multiplier method

$$\delta\, \ell n\, w - \alpha \sum_i \delta n_i - \beta \sum \in_i \delta n_i = 0$$

For most proable state $\delta \ln w = 0$

$$\sum_i \left[\ell n \frac{n_i + g_i}{n_i} - \alpha - \beta \in_i \right] \delta n_i = 0$$

$$\ell n \frac{n_i + g_i}{n_i} - \alpha - \beta \in_i = 0$$

$$\ell n \frac{n_i + g_i}{n_i} = \alpha + \beta \in_i \quad \text{or} \quad \ell n \left[1 + \frac{g_i}{n_i} \right] = \alpha + \beta \in_i$$

$$1 + \frac{g_i}{n_i} = e^{\alpha + \beta \in_i} \Rightarrow \frac{g_i}{n_i} = e^{\alpha + \beta \in_i} - 1$$

$$\boxed{\frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \in_i} - 1} = f_{BE}} \quad \ldots (1)$$

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Eq$^{n.}$ (1) represent the mean occoupation no. for a level of energy $\in_i$ or probability of occoupation or most proable distribution function or average of particle per level for ith cell

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$$f_{MB} = 1/e^{\alpha + \beta \in_i}$$

$$f_{FD} = 1/e^{\alpha + \beta \in_i} + 1$$

In general $$f = \frac{1}{e^{\alpha + \beta \in_i} + a}$$

$a = 0$ for M.B

$a = 1$ for F.D

$a = -1$ for B.E

Grand canonical partition function for F.D. (Fermi-Dirac distribution), B.E. (Bose-Einstein distribution) and M.B. (Mascwell-Boltzmann distribution).

Single state grand canonical partition function for F.D.:

$$\sum_{N_f} e^{-\alpha N_r - \beta E_s} = 1 + e^{\frac{\mu}{k_B T} - \frac{\epsilon s}{k_B T}} = 1 + e^{\frac{\mu - \epsilon_s}{k_B T}}$$

Total grand canonical partition function for F.D.

$$\boxed{Z(\mu, V, T) = \prod_s \left(1 + e^{\frac{\mu - \epsilon_s}{k_B T}}\right)}$$

Single state grand canonical partition function for B.E

$$\sum_{N_r} e^{-\alpha N_r - \beta E_s} = 1 + e\frac{\mu - \epsilon_s}{k_B T} + e\frac{2(\mu - \epsilon_s)}{k_B T} + e\frac{3(\mu - \epsilon_s)}{k_B T}$$

Total grand canonical partition function for B.E

$$Z(\mu, V, T) = \prod_s \left(1 - e^{\frac{\mu - \epsilon_s}{k_B T}}\right)^{-1} = \prod_s \left(1 - Ze^{-\beta E_s}\right)^{-1}$$

If $Ze^{-\beta E_s} >> 1$ then the series is infinite so $Ze^{-\beta E_s} < 1$

$$Z(\mu, V, T) = \prod_s \left(1 + Ze^{\beta E_s}\right)$$

Single state grand canonical P.F. (Partition Function) for M.B

$$= \sum_{N_r=0}^{\infty} z^{N_r} Q N_r(V,T) \sum_{N_r=0} \frac{z^{N_r} V^N}{N! \lambda^{3N}} = \exp \frac{zV}{\lambda^3} \rightarrow \text{for indistinguishable}$$

$$= \sum_{N_r=o}^{\infty} \frac{z^{N_r} V^N}{\lambda^{3N}} \rightarrow \text{for distinguishable case}$$

$$S = -k_B \sum_{r,S}^{\infty} P_{rs} \ell n P$$

$$P_{r,s} = e^{\frac{\mu N_r - \beta E_s}{k_B T}} / Z(z, V, T)$$

$$S = -k_B \sum_{r,s}^{\infty} \frac{e^{\frac{\mu N_r - \beta E_s}{k_B T}}}{Z(z,V,T)} \left[(\mu N_r = E_S)\beta - \ell n\, Z(z,V,T)\right]$$

$$= -k_B \left[\sum_{r,s} \mu\beta N_r \frac{e^{\frac{\mu N_r - \beta E_S}{k_B T}}}{Z(z,V,T)} - \sum_{r,s} \frac{\beta E_s e^{\frac{\mu N_r - \beta E_s}{k_B T}}}{Z(z,V,T)} - \sum_{r,s} \frac{e^{(\mu N_r - E_s)\beta}}{Z(z,V,T)} \ell n\, Z(z,V,T)\right.$$

But $\sum_{r,s} e^{(\mu N_r - E_s)\beta} = Z(z,V,T)$

$$S = -k_B \left[\mu\beta\bar{N} - \beta\bar{E}_s - \ell n\, Z(z,V,T)\right] = -\mu k_B \beta\bar{N} + k_B\beta\bar{E} + k_B \ell n\, Z(z,V,T)$$

$$= -\frac{\mu\bar{N}}{T} + \frac{U}{T} + k_B \ell n\, Z(z,V,T)$$

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The Grand canonical potential is defined as

$$\Omega = U - TS - \mu\bar{N}$$

Comparing $(\times)$ and $(\times\times)$ we get

$$\Omega = -k_B T \ \ell n \ Z\ (z,V,T)$$

Now $d\Omega = -SdT - \bar{N}d\mu - PdV$

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{\mu,V} \qquad \bar{N} = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V} \qquad P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}$$

Ideal Bose- Einstein gas :

Consider a B.E gas of N atom. Let these particle be distributed among states such that there are $n_1, n_2 \ldots\ldots n_i$ number of particle in quantum state whose energies are $\epsilon_1, \epsilon_2 \ldots\ldots \epsilon_i$ respectively

most probable distribution function for B.E gas

$$f = \frac{1}{e^{\alpha+\beta\epsilon_i} - 1}$$

Let the interaction between the particle is assumed to be neglibible so that the energy may be regarded entirely of translational character As translational levels are closely spaced so we will represent the summation by integration

$$g(\epsilon)d\epsilon = g_s \frac{2\pi V(2m)^{3/2}}{h^3} \epsilon^{1/2} d\epsilon$$

$g_s = (2S+1)$ = spin degeneracy factor

The number of particle having energy between ϵ and $\epsilon + d\epsilon$

$$N(\epsilon)d\epsilon = \frac{g_s 2\pi V(2m)^{3/2}}{h^3} \frac{\epsilon^{1/2} d\epsilon}{e^{\alpha+\beta\epsilon} - 1}$$

Total number of particle in the system

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\alpha} e^{\beta E} - 1} \quad \ldots (1)$$

Now,

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$$\Omega = -k_B T \ \ell n \ Z\ (\mu,V,T)$$

$$V - TS - \bar{N}\mu = -k_B T \ \ell n \ Z(\mu,V,T)$$

$$-PV = -k_B T \ \ell n \ Z(\mu,V,T)$$

$$\Omega = -k_B T \ \ell n \prod_s \left(1 - e^{-\alpha} e^{-\beta E_s}\right)$$

$$= -k_B T \sum_s \ell n \left(1 - e^{-\alpha} e^{-\beta E_s}\right)$$

$$= -k_B T \frac{2\pi g_s V(2m)^{3/2}}{h^3} \int \epsilon^{1/2} \ \ell n \ \left(1 - e^{-\alpha} e^{-\beta E}\right) dE$$

$$= -k_B T \frac{2\pi g_s V(2m)^{3/2}}{h^3} \left[\ell n \left(1 - e^{-\alpha-\beta\epsilon}\right) \frac{\epsilon^{3/2}}{\frac{3}{2}} \right]_0^\infty - \int \frac{1}{1 - e^{-\alpha-\beta\epsilon}} \times -e^{-\alpha-\beta\epsilon} \times \beta\epsilon^{3/2} \times \frac{2}{}$$

$$\Omega = -\frac{2}{3}\frac{2\pi g_s V(2m)^{3/2}}{h^3}\int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon}-1}d\epsilon \qquad \ldots(2)$$

$$U = \int \bar{\epsilon}\, N(E)\,dE = 2\pi g_s V(2m)^{3/2}\int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon}-1} \qquad \ldots(3)$$

Comparing eqn (2) and (3)

$$\Omega = -\frac{2}{3}U = -PV \quad \Rightarrow \quad \boxed{PV = \frac{2}{3}U}$$

$$U = 2\pi g_s V\frac{(2\pi m)^{3/2}}{h^3}k_B T\int_0^\infty \frac{\epsilon^{3/2}}{e^{\alpha+\beta\epsilon}-1}d\epsilon$$

Let $\frac{\epsilon}{k_B T} = x \quad \Rightarrow \quad d\epsilon = k_B T dx$

$$U = \frac{2\pi g_s V(2mk_B T)^{3/2}}{h^3}k_B T\int_0^\infty \frac{x^{3/2}}{e^\alpha e^x - 1}dx$$

Now $\int_0^\infty \frac{x^{3/2}}{e^\alpha e^x - 1} = \int_0^\infty \frac{x^{3/2}e^{-x}}{e^\alpha}\left(1-\frac{e^{-x}}{e^x}\right)^{-1}dx \qquad \{\because (1-x)^{-1} = 1+x+x^2;\ x \ll 1\}$

$$\int_0^\infty x^{3/2}\frac{e^{-x}}{e^x}\left(1+\frac{e^{-x}}{e^x}+\frac{e^{-2x}}{e^{2x}}+\ldots\right) = \int x^{3/2}\frac{e^{-x}}{e^x}dx + \int x^{3/2}\frac{e^{-2x}}{e^{2\alpha}}dx + \int x^{3/2}\frac{e^{-3x}}{e^{3\alpha}}dx$$

(Formula - $\int_0^\infty e^{-\alpha x}x^n = \frac{\Gamma(n+1)}{\alpha^{n+1}}$)

$$= \frac{1}{e^\alpha}\frac{\Gamma\left(\frac{5}{2}\right)}{1\frac{5}{2}} + \frac{1}{e^{2\alpha}}\frac{\Gamma\left(\frac{5}{2}\right)}{2\frac{5}{2}} + \frac{1}{e^{3\alpha}}\frac{\Gamma\left(\frac{5}{2}\right)}{3\frac{5}{2}} + \ldots$$

$$= \frac{3}{4}\sqrt{\pi}\left(\frac{1}{e^\alpha} + \frac{1}{e^{2\alpha}2^{5/2}} + \frac{1}{e^{3\alpha}3^{5/2}} + \ldots\ldots\right.$$

Now $U = \frac{2g_s V}{\sqrt{\pi}}\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2}k_B T\int_0^\infty \frac{x^{3/2}}{e^\alpha e^x - 1}dx \qquad \left(Z_t = V\left(\frac{2\pi mk_B T}{h^2}\right)^{3/2}\right.$

$$U = \frac{2g_s}{\sqrt{\pi}}Z_t k_B T \times \frac{3}{4}\sqrt{\pi}\left[\frac{1}{e^\alpha}+\frac{1}{e^{2\alpha}2^{5/2}}+\frac{1}{e^{3\alpha}3^{5/2}}+\ldots..\right]$$

$$= \frac{3}{2}g_s Z_t\, k_B T\left[\frac{1}{e^\alpha}+\frac{1}{e^{2\alpha}}2^{5/2}+\frac{1}{e^{3\alpha}3^{5/2}}+\ldots.\right]$$

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From equation (1),

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^E \frac{\epsilon^{1/2}\, d\epsilon}{e^{\alpha} e^{\beta\epsilon} - 1}$$

$$= g_s Z_t \left[\frac{1}{e^{\alpha}} + \frac{1}{e^{2\alpha} 2^{3/2}} + \frac{1}{e^{3\alpha} 3^{3/2}} + \ldots\ldots \right]$$

$$U = \frac{3}{2} N k_B T \left[\frac{1}{e^{\alpha}} + \frac{1}{e^{2\alpha} 2^{5/2}} + \frac{1}{e^{3\alpha} 3^{5/2}} + \ldots\ldots \right] \left[\frac{1}{e^{\alpha}} + \frac{1}{e^{2\alpha} 2^{3/2}} + \frac{1}{e^{3\alpha} 3^{3/2}} + \ldots\ldots \right]^{-1}$$

Now,
$$U = \frac{3}{2} N k_B T \left[1 - \frac{1}{e^{\alpha} 2^{5/2}} + \frac{1}{e^{2\alpha} 3^{5/2}} + \ldots\ldots \right] \left[1 - \frac{1}{e^{\alpha} 2^{3/2}} - \frac{1}{e^{2\alpha} 3^{3/2}} - \ldots\ldots \right]$$

$$= \frac{3}{2} N k_B T \left[1 - \frac{1}{e^{\alpha} 2^{5/2}} - \frac{1}{e^{2\alpha} 3^{5/2}} - \ldots\ldots \right]$$

So we are not obtaining the U as in classical ideal gas. Its value will decrease by some factor.

$$\Omega = -k_B T \ln Z(z, V, T) = \frac{2}{3} U = -PV$$

$$\Omega = U - TS - \mu N = U - TS - G = U - TS - A - PV = -PV \quad \ldots (1)$$

$$P = \frac{2}{3} \frac{U}{V}$$

This is same as in case of ideal gas.

$$I = \frac{2}{3} \frac{U}{V} = \frac{N k_B T}{V} \left[1 - \frac{1}{e^{\alpha} 2^{5/2}} - \frac{1}{e^{\alpha} 3^{5/2}} - \ldots\ldots \right] \quad \ldots (2)$$

From eqn (1) and (2) it is clear that there are deviation in energy and pressure from the values of classical ideal gas. The deviation from the perfect gas behaviour executed by B E gas is termed as degeneracy

Comparing (1) and (2)

$$\frac{1}{e^{\alpha}} = \frac{h^3}{g_s \left(2\pi m k T \right)^{3/2}} = \frac{N\lambda^3}{V g_s} - \text{degeneracy}$$

discriminant factor

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Q. 78. Free energy of a photon gas enclosed in a volume V is given by $F = -\frac{1}{3} aVT^4$, where *a* is the constant and T is the temperature of the gas. Find the chemical potential of the photon gas.

Soln. $F = U - TS$

$dF = dU - TdS - SdT$

$dF = dU - dU - PdV + \mu\, dN - SdT$

$= -SdT - PdV + \mu\, dN$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \frac{\partial}{\partial N} \left(-\frac{1}{3} a v T^4 \right) = 0 .$$

Problems that appeared in GATE from this section :

G-1. **The free energy of a photon gas enclosed in a volume V is given by $F = -1/3\ aVT^{-4}$, where a is a constant and T is the temperature of the gas. The chemical potential of the photon gas is**

(a) zero **(b)** $\frac{4}{3}aVT^3$ **(c)** $\frac{1}{3}aT^{-4}$ **(d)** aVT^{-4}

[GATE-2006]

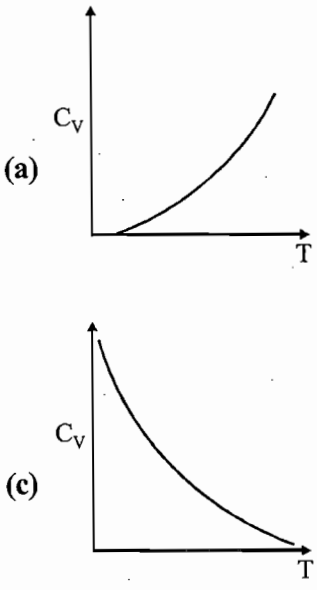
Soln. $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T}$; for this case $F = -\frac{1}{3}aVT^{-4}$ which is independent of N. Therefore, $\mu = 0$. Anyway, for photon gas (in equilibrium) $\mu = 0$.

Hence, the correct option is (a).

Common Data for Questions G-2 and G-3:

The partition function for a gas of photons is given by $\ell n\, Z = \frac{\pi^2}{45}\frac{V(k_BT)^3}{\hbar^3c^3}$

G-2. **The specific heat of the photon gas veries with temperature as**



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[GATE-2010]

Soln. Here, $\log Z = \frac{\pi^2}{45}V\frac{(k_BT)^3}{\hbar^3c^3}$

Putting $k_BT = \frac{1}{\beta}$, we get $\log Z = \frac{\pi^2}{45}\frac{V}{\hbar^3c^3}\frac{1}{\beta^3}$

$$U = -\frac{\partial}{\partial\beta}\log Z = -\frac{\pi^2}{45}\frac{V}{\hbar^3c^3}\frac{(-3)}{\beta^4} = \frac{\pi^2}{15}\frac{V}{\hbar^3c^3}(k_BT)^4 \quad \because \beta = \frac{1}{k_BT}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{4\pi^2}{15}\frac{Vk_B^4}{\hbar^3c^3}T^3$$

$$\Rightarrow C_V \propto T^3$$

Hence correct option is (b).

G-3. The pressure of the photon gas is

(a) $\frac{\pi^2}{15}\frac{V(k_BT)^3}{\hbar^3c^3}$ (b) $\frac{\pi^2}{8}\frac{V(k_BT)^4}{\hbar^3c^3}$ (c) $\frac{\pi^2}{45}\frac{V(k_BT)^4}{\hbar^3c^3}$ (d) $\frac{\pi}{45}\frac{V(k_BT)^{3/2}}{\hbar^3c^3}$

[GATE-2010]

Soln. $p=\frac{\log Z}{\beta}=k_BT\times\frac{\pi^2}{45}\frac{V(k_BT)^3}{\hbar^3c^3}=\frac{\pi^2}{45}\frac{V(k_BT)^4}{\hbar^3c^3}$

Hence correct option is (c).

G-4. The free energy for a photon gas is given by $F=-\left(\frac{a}{3}\right)VT^4$, where *a* is a constant. The entropy S and the pressure P of the photon gas are

(a) $S=\frac{4}{3}aVT^3, P=\frac{a}{3}T^4$ (b) $S=\frac{1}{3}aVT^4, P=\frac{4a}{3}T^3$

(c) $S=\frac{4}{3}aVT^4, P=\frac{a}{3}T^3$ (d) $S=\frac{1}{3}aVT^3, P=\frac{4a}{3}T^4$

[GATE-2007]

Soln. $F=-\frac{a}{3}VT^{-4}$

$P=-\left(\frac{\partial F}{\partial V}\right)_T=\frac{a}{3}T^4$

$S=\left(\frac{\partial F}{\partial T}\right)_V=\frac{4}{3}aVT^3$

Hence correct option is (a).

G-5. A photon gas is at thermal equilibrium at temperature T. The mean number of photons in an energy state $\varepsilon=\hbar\omega$ is:

(a) $\exp\left(\frac{\hbar\omega}{k_BT}\right)+1$ (b) $\exp\left(\frac{\hbar\omega}{k_BT}\right)$ (c) $\left[\exp\left(\frac{\hbar\omega}{k_BT}\right)\right]^{-1}$ (d) $\left[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right]^{-1}$

[GATE-2008]

Soln. The mean occupation number or the average number of particles in a state with energy ε is given by

$$\bar{n}=\frac{1}{\exp\left[(\varepsilon-\mu)/k_BT\right]\pm1}$$

where, '+' sign is for Fermi-Dirac distribution and '–' sign is for Bose-Einstein distribution.
Since, photon is a Boson, we must use '–' sign.
Also for photon $\mu=0$.

$$\therefore\quad \bar{n}_{\text{photon}}=\frac{1}{\exp\left(\frac{\varepsilon}{k_BT}\right)-1}=\left[\exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right]^{-1}\qquad(\because\ \varepsilon=\hbar\omega)$$

Hence correct option is (d).

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G-6. The partition function of two Bose particles each of which can occupy any of the two energy levels 0 and ε is:

(a) $1+e^{-2\varepsilon/kT}+2e^{-\varepsilon/kT}$ **(b)** $1+e^{-2\varepsilon/kT}+e^{-\varepsilon/kT}$ **(c)** $2+e^{-2\varepsilon/kT}+e^{-\varepsilon/kT}$ **(d)** $e^{-2\varepsilon/kT}+e^{-\varepsilon/kT}$

[GATE-2005]

Soln. $Z=\sum e^{\frac{-\epsilon_i n_i}{kT}}=e^{\frac{-0\times 2}{kT}}+e^{\frac{-\varepsilon}{kT}\times 2}+e^{\frac{-\varepsilon}{kT}}=e^{0}+e^{-2\varepsilon/kT}+e^{-\varepsilon/kT}=1+e^{-2\varepsilon/kT}+e^{-\varepsilon/kT}$

Hence correct option is (b).

STRONG DEGENERATE BOSON GAS (BOSE-EINSTEIN CONDENSATION)

Chemical potential for Boson gas is always negative. The average no. of particle in the s^{th} particle state of energy ϵ_s is given by

$$f(\epsilon_s)=\frac{1}{e^{\frac{\epsilon_s-\mu}{k_BT}}-1}$$

As the total no. of particles in Boson gas is fixed. So μ must increase as T decrease keeping volume constant, to keep $f(\epsilon_s)$ +ve consequently $\mu \to 0$. The no. of particle in ground state increases sharply. This macroscopic occoupation of the ground state is called Bose-Einstein condensation. At very low temperature the value of μ is very close to the ground state energy i.e zero.

At $T = T_B$

$$\frac{N}{V}=\frac{2\pi g_S(2mk_BT)^{3/2}}{h^3}\int_0^\infty \frac{x^{1/2}dx}{e^{\alpha}e^{x}-1}$$

$$\int_0^\infty \frac{x^{1/2}dx}{e^{x}-1}=\frac{\sqrt{\pi}}{2}\left[1+\frac{1}{2^{3/2}}+\frac{1}{3^{3/2}}+\cdots\right]=\frac{\sqrt{\pi}}{2}\xi\left(\frac{3}{2}\right)\quad\left(\xi\left(\frac{3}{2}\right)=2.612\right)$$

$$\frac{N}{V}=\frac{2\pi g_s}{h^3}(2mk_BT_B)^{3/2}\frac{\sqrt{\pi}}{2}\xi\left(\frac{3}{2}\right)=g_s\left(\frac{2\pi mk_BT_B}{h^2}\right)^{3/2}\xi\left(\frac{3}{2}\right)$$

$$\boxed{T_B=\frac{h^2}{2\pi mk_B}\left[\frac{N}{V g_s\xi(3/2)}\right]^{2/3}}$$

$$T_B=0.084\ \frac{h^2}{mk_B}\left[\frac{N}{Vg_s}\right]^{2/3}$$

This is called condensation temperature, degeneracy temperature or characterstic temperature or Bose temperature or transitition temperature. The condition for onset of Bose-Einstein gas (starting) is

$$N > VT^{3/2}\left(\frac{2\pi mk_BT}{h^3}\right)^{3/2}\xi\left(\frac{3}{2}\right)$$

$$N = N_0 + Ne$$

$N_0 \to$ number of particle in the ground state

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Ne → no of particle distributed over excited state

$$N_e = N\left(\frac{T}{T_B}\right)^{3/2}$$

$$N_0 = N - Ne = N\left[1-\left(\frac{T}{T_B}\right)^{3/2}\right]$$

At $T < T_B$ the system may be looked upon as a mixture of two phase

(i) Normal phase consisting Ne particle distributed over excited state ($\epsilon \neq 0$)

(ii) Condensed phase consisting of no particle accumulated in the ground state ($\epsilon = 0$)

$$U = \frac{3}{2}N_e k_B T \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{5}{2}\right)}$$

$$= \frac{3}{2}N\left(\frac{T}{T_B}\right)^{3/2} k_B T \frac{\xi\left(\frac{5}{2}\right)}{\xi\left(\frac{5}{2}\right)}$$

$$U = \frac{3}{2}\,Nk_BT\left(\frac{T}{T_B}\right)^{3/2}\frac{1.342}{2.612}$$

$$= 0.5314 \times \frac{3}{2}\,Nk_BT\left(\frac{T}{T_B}\right)^{3/2}$$

$$PV = \frac{2}{3}U = 0.53\;\; Nk_BT\left(\frac{T}{T_B}\right)^{3/2}$$

$$PV = 21.1\, g_s \frac{m^{3/2}}{h^3}(k_BT)^{5/2}$$

$P \alpha T^{5/2}$ but independent of r and V only for $T < T_B$

The Bose - Einstein condensation take place in momentum space.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 1.925\;\; Nk_B\left(\frac{T}{T_B}\right)^{3/2}$$

$$N\mu = U - TS + PV$$

At $T < T_B$, $\mu = 0$

$$S = \frac{PV + U}{T} = \frac{5}{2}\,\frac{PV}{T}$$

$$S = \frac{5}{2} \times 0.51\;\; Nk_BT\left(\frac{T}{T_B}\right)^{3/2} \Rightarrow S = N_e\;\frac{5}{2} \times 0.51 k_B$$

$$S \alpha N_e,\; S \alpha \left(\frac{T}{T_B}\right)^{3/2}$$

At $T = T_B$ all the thermodynamic quantities

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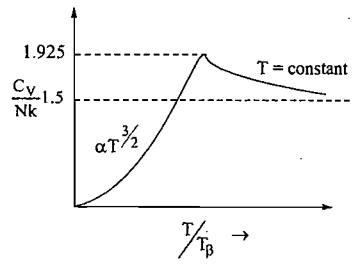
P, U, S, A, Ω and C_V are continuous but derivative of specific heat is discontinuous at $T = T_B$

As $T \to \infty$ all the thermodynamic value approach to their classical value

$$PV^{5/3} = \text{constant}, \qquad VT^{3/2} = \text{constant}$$

$$\frac{P}{T^{5/2}} = \text{constant}, \quad \gamma = \frac{C_P}{C_V}$$



This result is valid for Ideal Bose gas for reversible adiabatic process as for classical ideal gas but for ideal Bose gas $\frac{C_P}{C_V} = \gamma \neq \frac{5}{3}$ always. At $T >> T_B$ $\frac{C_P}{C_V} = \gamma = \frac{5}{3}$ but at any finite temperature γ is always greater than $\frac{5}{3}$.

Problems that appeared in GATE from this section :

G-1. Which of the following atoms cannot exhibit Bose-Einstein condensation, even in principle?
(a) $^1H_1$ (b) $^4He_2$ (c) $^{23}Na_{11}$ (d) $^{40}K_{19}$ [GATE-2010]

Soln. To exhibit Bose-Einstein condensation, particle must be a Boson $\Rightarrow$ Integral spin.
Since, all proton, neutron and electron have half integral spin, only those atoms whose $n_p + n_n + n_e$ is even will be a boson.
where

n_p = number of proton
n_n = number of neutron
n_e = number of electron

$= n_n$ = number of neutron = mass number.

For $^1H_1 : n_n + n_e = 1 + 1 = 2$ (even) (a)
For $^4He_2 : n_n + n_e = 4 + 2 = 6$ (even) (b)
For $^{23}Na_{11} : n_n + n_e = 23 + 11 = 34$ (even) (c)
For $^{40}K_{19} : n_n + n_e = 40 + 19 = 59$ (odd) (d)
So, $^{40}K_{19}$ cannot exhibit Bose-Einstein condensation.
Hence, the correct option is (d).

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G-2. Which of the following conditions should be satisfied by the temperature T of a system of N non-interacting particles occupying a volume V, for Bose-Einstein condensation to take place?

(a) $T < \frac{h^2}{2\pi m k_B}\left\{\frac{N}{V\xi\left(\frac{3}{2}\right)}\right\}^{1/3}$

(b) $T < \frac{h^2}{2\pi m k_B}\left\{\frac{N}{N\xi\left(\frac{3}{2}\right)}\right\}^{1/2}$

(c) $T < \frac{h^2}{2\pi m k_B}\left\{\frac{N}{V\xi\left(\frac{3}{2}\right)}\right\}^{1/2}$

(d) $T < \frac{h^2}{2\pi m k_B}\left\{\frac{N}{N\xi\left(\frac{3}{2}\right)}\right\}^{1/2}$

where m is the mass of each particle of the system, k_B is the Boltzmann constant, h is the Planck's constant and ξ is the well known Zeta function.

Soln. For Bose-Einstein condensation to take place the temperature of the Boson gas should be less than T_B. Where T_B is given by the following expression.

$$T_B = \frac{h^2}{2\pi mk}\left[\frac{N}{V\, g_s \xi\left(\frac{3}{2}\right)}\right]^{2/3}$$

Hence correct option is (a).

G-3. For an energy state E of a photon gas, the density of states is proportional to

(a) $\sqrt{E}$ **(b)** E **(c)** $E^{1/2}$ **(d)** E^2

[GATE-2001]

Soln. Density of states is defined as

$$D(E) = \frac{4\pi g p^2}{(2\pi\hbar)^3}\left(\frac{dp}{dE}\right)$$

where p = momentum of the particle.

For photons we have $E = pc \Rightarrow p^2 = \frac{E^2}{c^2}$ and $\frac{dp}{dE} = \frac{1}{c}$

$$\therefore\ D(E) = \frac{4\pi g E^2}{(2\pi\hbar c)^3} \Rightarrow D(E) \propto E^2$$

Hence correct option is (d).

G-4. In Bose-Einstein condensates, the particles

(a) habe strong interparticle attraction **(b) condense in real space**

(c) have overlapping wavefunctions **(d) have large and positive chemical potential**

[GATE-2015]

Soln. In Bose-Einstein condensate the condensation takes place in energy space hence option (a), (b) are wrong. Option (d) is also wrong since for Boson the chemical potential is always negative (zero for photon).

Hence correct option is (c).

IDEAL FERMI GAS

Ideal Fermi gas

$0 \le z < \infty$ – Ideal fermi gas

$0 < z < 1 \rightarrow$ – Ideal Bose gas z = fugacity

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$P = \frac{2}{3}\frac{U}{V} = \frac{2}{3}U$

If $\frac{n\lambda^3}{g} >> 1$ – Weakly degenerate Fermi gas

$\frac{n\lambda^3}{g} \rightarrow \infty \rightarrow$ – Completely degenerate or Strongly degenerate

Strongly degenerate or Completly degenerate ideal fermi gas

$$f(E) = \frac{1}{e^{\frac{\in -\mu}{k_B T}} + 1} = 1 \quad \text{for} \quad \in < \mu (= E_F)$$

$$= 0 \quad \text{for} \quad \in > \mu (= E_F)$$

Chemical potential at T = 0 is equal to Fermi energy

$\mu = E_f$, at $T = 0$ Fermi level is that level for which the occoupation no. $f(\in_i)$ is $\frac{1}{2}$

$N = \int_0^\infty f(E)g(E)dE$

For strongly degenerate

$$N = \int_0^{E_f} 1\times g(E)dE + \int_{E_f}^{\infty} 0\times g(E)dE$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^{E_f} g(E)dE$$

$$N = \frac{4}{3}\frac{\pi V g_s}{h^3}(2m)^{3/2} E_F^{3/2} \Rightarrow E_F = \frac{h^2}{2m}\left(\frac{3N}{4\pi V g_s}\right)^{3/2} \rightarrow \text{strongly degenerate Fermi gas}$$

2001]

For electron or proton $g_s = 2$

$$E_F = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{3/2} \quad \ldots (1)$$

g_s = (2S+1) multiplicity due to spin $E = \frac{p^2}{2m}$ $E_F = \frac{1}{2m}\left[h\left(\frac{3N}{4\pi V g_s}\right)^{\frac{1}{3}}\right]^2$

$$= \frac{\hbar}{2m}\left(\frac{6\pi^2 n}{g_s}\right)^{3/2} = 13.65\times10^{-19}\, n^{2/3} \text{ for electron}$$

P_F = Fermi momentum $\rightarrow$ $P_F = h\left(\frac{3N}{4\pi V g_s}\right)^{1/3}$ $E_F = k_B T_f$

2015]

T_f = Fermi temp or degenerate temp for fermi gas

rong.

So $$\boxed{T_f = \frac{1}{k_B}\frac{h^2}{2m}\left(\frac{3N}{4\pi V g_s}\right)^{2/3}}$$

Ground State Energy (E_0):

$$E_o = \int_0^{\infty} \in f(E)\, g(E)\, dE = \int_0^{E_F} \in f(E)\, g(E)dE + \int_0^{\infty} \in \times f(E)\, g(E)dE$$

$$= \int_0^{E_F} \in \times 1\times g(E)dE + \int_0^{\infty} (E=0)\times g(E)dE$$

$$= \int_0^{E_F} E\times g(E)dE$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_0^{E_F} \in^{3/2} dE$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \times \frac{2}{5} \in^{5/2} = \frac{4}{5}\frac{\pi V g_s (2m)^{3/2}}{h^2} E^{5/2}$$

Average ground state energy

$$\frac{E_0}{N} = \frac{\frac{4}{5}\pi V g_s (2m)^3\, 2\in^{5/2}}{h^3} \Big/ \frac{\frac{4}{3}\pi V g_s (2m)^{3/2}}{\in^{3/2}} = \frac{3}{5}E_F \qquad \Rightarrow \boxed{\frac{E_o}{N} = \frac{3}{5}E_f}$$

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Ground state pressure of the system P

$$P_o = \frac{2}{3} \frac{E_o}{V}$$

$$= \frac{2}{3} \times \frac{3}{5} \frac{N}{V} E_F = \frac{2}{5} n E_f$$

$$P_0 = \frac{2}{5} n E_f \qquad \Rightarrow P_0 = \left(\frac{6\pi^2}{g_s}\right)^{3/2} \frac{\hbar^2}{5m} n^{5/3}$$

$P_0 \alpha\, n^{5/3}$ $\qquad$ $P = 0$ for Bose gas

The zero point motion is clearly a quantum effect arising because of Pauli exclusion principle. According to which even at $T = 0$ the particles constituting the system can't accumulate into a single particle state (As can in B.E case) and are therefore spread over a requisite no. of lowest available energy state. As a result in Fermi system even at absolute zero quite exist.

The Fermi gas at finite temp but low (weekly degenerate) The no. of particle

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_o^\infty \frac{\epsilon^{1/2}}{e^{\frac{\epsilon-\mu}{k_B T}} + 1} d\epsilon \qquad \int_0^\infty \frac{Q(x)dx}{e^{x-\xi}+1} = \int_0^{\xi_1} Q(x)dx + \frac{\pi^2}{6}\left(\frac{\partial Q}{\partial x}\right)_{x=\xi} + \frac{7\pi^4}{360}\left(\frac{d^3Q}{\partial x^3}\right)_{x=\xi}$$

G-1.

For low temp we can expand the integral by approximation upto 1st order I compare these two and take $\frac{\epsilon}{k_B T} = 1$.

Soln

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3} \int_o^\mu \epsilon^{1/2} d\epsilon + \frac{\pi^2}{6}(k_B T)^2 \frac{1}{2}\mu^{-1/2}$$

$$= \frac{2\pi V g_s (2m)^{3/2}}{h^3} \frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_B T)^2 \frac{1}{2}\mu^{-1/2}$$

G-2.

$$= \frac{3N}{2E_f^{3/2}}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_B T)^2 \frac{1}{2}\mu^{-1/2}\right]$$

$$E_F^{3/2} = \frac{3}{2}\mu^{3/2}\left[\frac{2}{3} + \frac{\pi^2}{12}\left(\frac{k_B T}{\mu}\right)^2\right] \mu^{-3/2} \frac{1}{18}\pi^2\left(\frac{k_B T}{\mu}\right)^2$$

$$E_F(T) = E_F(0)\left[1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F(0)}\right)^2\right]$$

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Solr

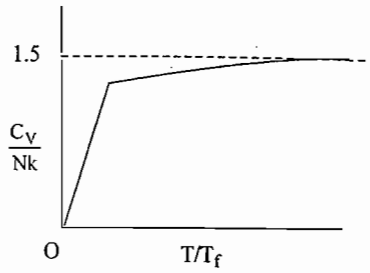
$$\frac{U}{N} = \frac{E}{N} = \frac{3}{5} E_F^{(0)}\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{E_f(0)}\right)^2\right]$$

$$P = \frac{2}{3}\frac{U}{V} = \frac{2}{5}\frac{N}{V} E_f(0)\left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{E_f(0)}\right)^2\right]$$

$$\frac{C_V}{Nk} = \frac{\pi^2}{2}\frac{k_B T}{E_f(0)} \rightarrow \text{electronic specific heat in case of solid}$$

$$\frac{A}{N} = \mu - \frac{PV}{N}$$

$$= \frac{3}{5} E_f(0) \left[1 - \frac{5\pi^2}{12} \left(\frac{k_B T}{E_f(0)} \right)^2 + \ldots\ldots \right]$$



$$\frac{S}{Nk_B} = \frac{\pi^2}{2} \frac{k_B T}{E_f}(0)$$

At $T \to 0$ $S \to 0$ in accordance with the third low of thermodynamics

For $T << T_f$ the specific heat varies as the first power of temperature morever in magnitude it is considerable smaller than the classical value $\frac{3}{2} Nk_B$.

Problems that appeared in GATE from this section :

G-1. The pressure for a non-interacting Fermi gas with internal energy U at temperature T is:

(a) $P = \frac{3}{2}\frac{U}{V}$ **(b)** $P = \frac{2}{3}\frac{U}{V}$ **(c)** $P = \frac{3}{5}\frac{U}{V}$ **(d)** $P = \frac{1}{2}\frac{U}{V}$

[GATE-2005]

Soln. For non-interacting Fermi-gas $\boxed{P = \frac{2}{3}\frac{U}{V}}$ which is also true for Boson and classical gas.

Hence correct option is (b).

G-2. A system of non-interacting Fermi particles with Fermi energy E_f has the density of states proportional to $\sqrt{E}$, where E is the energy of a particle. The average energy per particle at temperature T = 0 is:

(a) $\frac{1}{6}E_F$ **(b)** $\frac{1}{5}E_F$ **(c)** $\frac{2}{5}E_F$ **(d)** $\frac{3}{5}E_F$

[GATE-2005]

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Soln. We have in general $N = \int_0^{E_F} f(E)\, g(E)\, dE$; where $f(E)$ = Fermi distribution function and

$$\bar{E} = \int_0^{E_F} E\, f(E)\, g(E)\, dE.$$

Given : $g(E) \propto \sqrt{E}$

$$\therefore \quad N \sim \int_0^{E_f} f(E)\, E^{1/2} dE \approx F(E_F) \cdot \frac{2}{3} E_F^{3/2} \qquad \ldots(1)$$

Similarly $E \sim \int_0^{E_f} E\, f(E)\, E^{1/2} dE \approx F(E_F) \cdot \frac{2}{5} E_F^{5/2}$ ...(2)

$\left(\because \int E^{1/2}dE = \frac{2}{3}E^{3/2} \text{ and } \int E^{3/2}dE = \frac{2}{5}E^{5/2}\right)$

Now, average energy per particle $= \frac{\bar{E}}{N} = \frac{F(E_F)\frac{2}{5}E_F^{5/2}}{F(E_F)\frac{2}{3}E_F^{3/2}}$ (from (1) and (2))

$\Rightarrow \boxed{\frac{\bar{E}}{N} = \frac{3}{5}E_F}$; where $F(E_F)$: some funcation of E_F

Hence correct option is (d).

G-3. The specific heat of an ideal Fermi gas in 3-dimension at very low temperatures (T) varies as
(a) T (b) $T^{3/2}$ (c) T^2 (d) T^3.

[GATE-2004]

Soln. At low temperature, the fermions are confined to a degenerate state and for degenerate system at low temperature; specific heat is proportional to T.

Hence correct option is (a).

G-4. Consider the Fermi-Dirac distribution function f(E) at room temperature (300 K) where E refers to energy. If E_F is the Fermi energy, which of the following is true?
(a) f(E) is a step function
(b) $f(E_F)$ has a value of 1/2
(c) States with $E < E_F$ are filled completely
(d) f(E) is large and tends to infinity as E decreases much below E_F.

[GATE-2003]

Soln. $$f(E) = \frac{1}{\exp[(E - E_F)/kT + 1]}$$

For $E = E_F$

$$f(E_F) = \frac{1}{\exp[0] + 1} = \frac{1}{2}$$

Hence correct option is (b).

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G-5. The probability that a state which is 0.2 eV above the Fermi energy in a metal atom at 700 K is
(a) 96.2% (b) 62.5% (c) 3.5% (d) 37.7%

[GATE-2001]

Soln. We know that $f(E) = \frac{1}{\exp\left[\frac{E - E_F}{k_B T}\right] + 1}$

Here, $E = E_F + 0.2, t = 700\,K$

$$f(E) = \frac{1}{\exp\left[\frac{0.2 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 700}\right] + 1} = \frac{1}{\exp\left[\frac{32 \times 10^{-21}}{9.66 \times 10^{-21}}\right] + 1} = \frac{1}{\exp[3.31] + 1}$$

$$= \frac{1}{27.46 + 1} = \frac{1}{28.46} = 0.035$$

Hence correct option is (c).

G-6. For a Fermi gas of N particles in three-dimension at $T = 0\ K$, the Fermi energy E_F is proprotional to
(a) $N^{2/3}$ **(b)** $N^{3/2}$ **(c)** N^3 **(d)** N^2

[GATE-2009]

Soln. The Fermi energy is given by

$$E_F = \frac{\hbar^2}{2m}(3\pi^2 N)^{2/3}$$

$$\Rightarrow E_F \propto N^{2/3}$$

Hence correct option is (a).

Common data for Q.G-7, Q.G-8 and Q.G-9.

A system consists of three spin-half particles, the z components of whose spins $S_z(1), S_z(2)$ and $S_z(3)$ can take value $+1/2$ and –1/2. The total spin of the system is $S_z = S_z(1) + S_z(2) + S_z(3)$

G-7. **The total number of possible micro-states of this system is:**
(a) 3 **(b) 6** **(c) 7** **(d) 8**

[GATE-2003]

Soln. For each micro-state two spin orientation are possible one + 1/2 and – 1/2. Therefore, total number of micro-states with three spin components = $2^3 = 8$.
Hence correct option is (d).

G-8. **The total number of micro-states with $S_z = 1/2$ is:**
(a) 3 **(b) 5** **(c) 6** **(d) 7**

[GATE-2003]

Soln. For $S_z = 1/2$, the following configurations are possible

$$\text{I}: \begin{bmatrix} +1/2 & -1/2 & +1/2 \\ +1/2 & +1/2 & -1/2 \\ -1/2 & +1/2 & +1/2 \end{bmatrix} \begin{matrix} \\ \text{II}: \\ \text{III}: \end{matrix}$$

Hence correct option is (a).

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G-9. **Consider an ensemble of systems where each microstate has equal probability. The ensemble average of S_z is:**
(a) –1/2 **(b) 0** **(c) 1/2** **(d) 3/2**

[GATE-2003]

Soln. The following micro-states are possible

$S_z(1)$	$S_z(2)$	$S_z(3)$	S_z
+1/2	+1/2	+1/2	+3/2
+1/2	+1/2	−1/2	+1/2
+1/2	−1/2	−1/2	−1/2
−1/2	−1/2	−1/2	−3/2

Since each state is equally probable, only the above configurations are possible. Hence, ensemble average =

$$\frac{+\frac{3}{2}+\frac{1}{2}-\frac{1}{2}-\frac{3}{2}}{4}=0.$$

Hence correct option is (b).

G-10. The probability that an energy level ε at a temperature T is unoccupied by a fermion of chemical potential μ is given by

(a) $\frac{1}{e^{(\varepsilon-\mu)/k_BT}+1}$ **(b)** $\frac{1}{e^{(\varepsilon-\mu)/k_BT}-1}$ **(c)** $\frac{1}{e^{(\mu-\varepsilon)/k_BT}+1}$ **(d)** $\frac{1}{e^{(\mu-\varepsilon)/k_BT}-1}$

[GATE-2009]

Soln. The distribution function for fermions is given by $f(\varepsilon)=\frac{1}{\exp[(\varepsilon-\mu)/k_BT]+1}$.

Also, $f(\varepsilon)$ = probability that an energy level ε at a temperature T is occupied by a fermions of chemical potential μ.

$\therefore$ Probability than an energy level ε at temperature T is unoccupied by a fermions of chemical potential $\mu = 1-f(\varepsilon)$.

($\because$ Probability of unoccupancy = 1 – probability of occupancy)

$\Rightarrow$ Required probability $= 1-f(\varepsilon)=1-\frac{1}{\exp[(\varepsilon-\mu)/k_BT]+1}$

$$=\frac{\exp[(\varepsilon-\mu)/k_BT]+1-1}{\exp[(\varepsilon-\mu)/k_BT]+1}=\frac{\exp[(\varepsilon-\mu)/k_BT]}{\exp[(\varepsilon-\mu)/k_BT]+1}$$

Dividing numerator and denominator by $\exp[(\varepsilon-\mu)/k_BT]$, we get the required

$$\text{probability}=\frac{1}{1+1/\exp[(\varepsilon-\mu)/k_BT]}=\frac{1}{\exp[(\mu-\varepsilon)/k_BT]+1}$$

Hence correct option is (c).

G-11. For a two-dimensional free electron gas, the electronic density n, and the Fermi energy E_F, are related by

(a) $n=\frac{(2mE_F)^{3/2}}{3\pi^2\hbar^2}$ **(b)** $n=\frac{mE_F}{\pi\hbar^2}$ **(c)** $n=\frac{mE_F}{2\pi\hbar^2}$ **(d)** $n=\frac{2^{3/2}(mE_F)^{1/2}}{\pi\hbar}$

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[GATE-2010]

Soln. From definition we have $n=\int_0^{E_F} g(E)\,f(E)\,dE$ such that $f(E)=\begin{cases}0;\ E>E_F\\ 1;\ E\le E_F\end{cases}$

(for free electron gas)

$f(E)$: distribution function.

$g(E)$: density of states.

For 2-dimension, we have $g(E)\,dE=\frac{2\pi m}{h^2}\,dE$

$$\therefore\quad n=\int_0^{E_F}\frac{2\pi m}{h^2}\,dE=\frac{2\pi mE}{h^2}\Big|_0^{E_F}=\frac{m\,E_F}{2\pi\frac{h^2}{2\pi\cdot 2\pi}}=\frac{m\,E_F}{2\pi\,\hbar^2}$$

Hence correct option is (c).

Common data for Q.G-12 and Q.G-13.

Consider two dimentional electron gas of N electrons of mass 'm' each in a system of size L×L.

G-12. The density of states between energy ε and $\varepsilon + d\varepsilon$ is

(a) $\frac{4\pi L^2 m}{h^2}$ **(b)** $\frac{4\pi L^2 m}{h^2}\frac{1}{\sqrt{\varepsilon}}$ **(c)** $\frac{4\pi L^2 m}{h^2}\sqrt{\varepsilon}$ **(d)** $\frac{4\pi L^2 m}{h^2}\varepsilon$

[GATE-2008]

Soln. Number of states in phase space volume (in two-dimension) $= g\frac{d^2r\,d^2p}{(2\pi\hbar)^2}$

where, $(2\pi\hbar)^f$ = volume of phase space containing 1 microstate.

Integrating the number of states in configuration space we get, number of states $= g\frac{V\,d^2p}{(2\pi\hbar)^2} = g\frac{V\,2\pi p\,dp}{(2\pi\hbar)^2}$

$\Rightarrow \quad \mathcal{D}(\varepsilon)\,d\varepsilon = g\frac{V\,2\pi m\,d\varepsilon}{(2\pi\hbar)^2} = \frac{4\pi L^2 m\,d\varepsilon}{h^2}.$ ($\because$ for electrons $g = 2$ and $V = L^2$ given)

Hence correct option is (a).

G-13. The ground state energy E_0 of the system in terms of the Fermi energy E_F and the number of electrons N is given by

(a) $\frac{1}{3}NE_F$ **(b)** $\frac{1}{2}NE_F$ **(c)** $\frac{2}{3}NE_F$ **(d)** $\frac{3}{5}NE_F$

[GATE-2008]

Soln. For ideal Fermi gas (since electron is a fermion), $E_0 = \frac{3}{5}NE_F$ always.

Hence correct option is (d).

G-14. For an ideal Fermi gas in three-dimensions, the electron velocity v_F at the Fermi surface is related to electron concentration *n* as

(a) $v_F \propto n^{1/2}$ **(b)** $v_F \propto n$ **(c)** $v_F \propto n^{2/3}$ **(d)** $v_F \propto n^{1/3}$

[GATE-2012]

Soln. Fermi energy

$E_F = \frac{1}{2}mv_F^2 = \frac{\hbar^2}{2m}(2\pi^2 n)^{2/3}$ or $v_F^2 \propto n^{2/3}$ or $v_F \propto n^{1/3}$

Hence correct option is (d).

G-15. The total energy, E of an ideal non-relativistic Fermi gas in three dimensions is given by $E \propto \frac{N^{5/3}}{V^{2/3}}$

where N is the number of particles and V is the volume of the gas. Identify the CORRECT equation of state (P being the pressure),

(a) $PV = \frac{1}{3}E$ **(b)** $PV = \frac{2}{3}E$ **(c)** $PV = E$ **(d)** $PV = \frac{5}{3}E$

[GATE-2012]

Soln. Let, $E = \frac{K}{V^{2/3}}$ ...(i)

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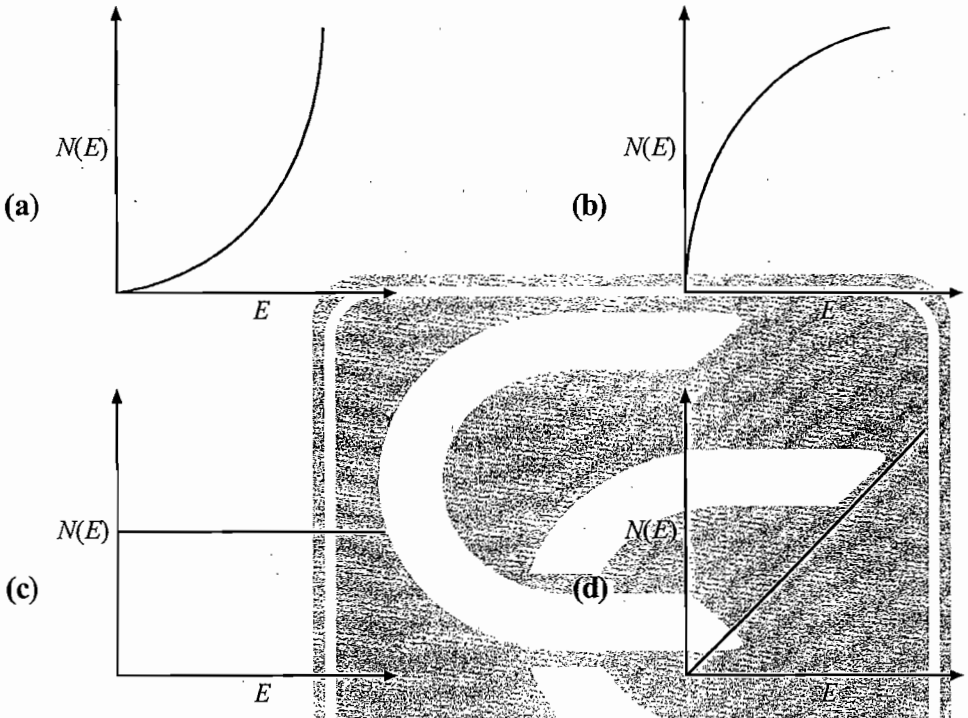
Now, $P = -\dfrac{\partial E}{\partial V} = -\dfrac{\partial}{\partial V}\left(\dfrac{K}{V^{2/3}}\right) = \dfrac{2}{3}KV^{-5/3} = \dfrac{2}{3}\dfrac{K}{V^{5/3}}$ or $P = \dfrac{2K}{3V \times V^{2/3}}$

$PV = \dfrac{2}{3}\dfrac{K}{V^{2/3}} = \dfrac{2}{3}E$ [Using equation (i)]

Hence correct option is (d).

G-16. For a free electron gas in two-dimensions, the variation of the density of states, $N(E)$ as a function of energy E, is best represented by



[GATE-2014]

Soln. For free electron gas in two dimensions, the density of states $N(E)$ has following property $N(E)\,dE \propto d^2p$.

Now, $d^2p = 2\pi p\,dp$

Since, $p^2 = 2mE \Rightarrow 2p\,dp = 2m\,dE$

$\Rightarrow 2p\pi\,dp = 2\pi m\,dE \equiv d^2p$

$\therefore N(E)\,dE \propto 2\pi m\,dE$

$\Rightarrow N(E)$ is independent of E.

Hence correct option is (c).

G-17. The energy dependence of the density of states for a two dimensional non-relativistic electron gas is given by, $g(E) = CE^n$, where C is constant. The value of n is_____.

[GATE-2015]

Soln. For a two dimensional non-relativistic electron gas the density of states is given by

$$g(E)dE = 2\frac{V\,d^2p}{(2\pi\hbar)^2} = 2\frac{V\,2\pi p\,dp}{(2\pi\hbar)^2} = 2\frac{V\,2\pi m\,dE}{(2\pi\hbar)^2}.$$

Thus, $g(E)$ is independent of E

$\Rightarrow g(E) = CE^0$. **Hence the value of n is zero.**

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G-18. **The number of states for a system of N identical free particles in a three dimensional space having total energy between E and $E+\delta E(\delta E << E)$, is proportional to**

(a) $\left(E^{\frac{3N}{2}-1}\right)\delta E$ **(b)** $E^{\frac{N}{2}}\delta E$ **(c)** $NE^{\frac{1}{2}}\delta E$ **(d)** $E^{N}\delta E$

[GATE-2005]

Soln. The number of states in the energy range E and E + dE is given by

$$g(E)dE = g_s \frac{4\pi V}{h^3} 2mE\sqrt{\frac{m}{2E}}dE \quad ...(i)$$

But $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1}$ ...(ii)

From equation (i) and (ii) the number of particles in range ε and $\varepsilon + d\varepsilon$ is

$$dn(\varepsilon) = g_i \frac{h^3}{D} \frac{\sqrt{2m}NE^{1/2}dE}{e^{\varepsilon/k_BT}+1}$$

Hence, $dN(\varepsilon) \propto NE^{1/2}dE$

Hence correct option is (c).

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Comparison of MB, BE and FD-statistics :

S.No.	Features	MB	BE	FD
1.	Particles	Distinguishable, the uncertainty relation and the Pauli's exclusion principle do not apply. Ex: gas particles at ordinary temp.	Indistinguishable, called bosons that do not obey Pauli's exclusion principle but obey uncertainty relation. Ex: photon and phonon gas.	Indistinguishable, called fermions that obey Pauli's exclusion principle and also the uncertainty relation Heisenberg. Ex: electron gas in metals.
2.	Particle spin	Spinless	0, 1, 2, ...	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots$
3.	Number of ways W in which N particle could be distributed in the g states.	$(g)^N$	$\frac{(N+g-1)!}{N!(g-1)!}$	$\frac{g!}{N!(g-N)!}$
4.	Wave function, ψ		Symmetric under interchange of the coordinates of any two bosons.	Antisymmetric on interchange of the coordinates of any two fermions
5.	Number of particles energy state	No upper limit	No upper limit per quantum state, as Pauli principle is not obeyed.	At best, only one per quantum state is allowed as Pauli principle is obeyed.
6.	Distribution function	$f(E) = e^{-E/kT}$	$f(E) = \frac{1}{e^{\alpha} e^{E/kT} - 1}$	$f(E) = \frac{1}{e^{(E-E_F)/kT} + 1}$
7.	Total energy	$U = \frac{3}{2} NkT$	$\frac{3}{2} NkT \left(1 - \frac{1}{2^{5/2} e^{-\alpha}}\right)$	$\frac{3}{2} NkT \left(1 + \frac{1}{2^{5/2} e^{-\alpha}}\right)$
8.	Pressure	$p = \frac{NkT}{V}$	$\frac{NkT}{V}\left(1 - \frac{1}{2^{5/2} e^{-\alpha}}\right)$	$\frac{NkT}{V}\left(1 + \frac{1}{2^{5/2} e^{-\alpha}}\right)$

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Chapter 8

Physics of Black-Body Radiation & Phase Transition

Prevost's theory of heat exchange :

According to this theory all bodies radiate thermal radiation at all temperature. The amount of thermal radiation radiated per unit time depends on the nature of emitting surface, its area and temperature. The rate is faster at high temperatue. Beside a body also absorbs a part of the thermal radiation emitted by the sorrounding bodies when the radiations falls on it at a rate depending on the surface and temperature of the sorrounding bodies. If a body radiates more than what it absorbs its temperature falls. If a body radiates less than what it absorbs its temperature rises

Note :

1. When the temp of a body is equal to the temperature of its sorroundings it radiates at the same rate as it absorbs
2. The thermal equilibrium between any body and its sorrounding is dynamical equilibrium.
3. The radiation inside an encloser is homogeneous and isotropic
4. The radiation inside a uniform temperature encloser depends only on the temperature and not on the nature of the walls of the encloser or on the bodies present inside it.
5. The radiation inside on encloser is identical with the radiation emitted by a perfectly black body at same temperature.

Black body radiation : A body that absorbs all the radiation of any wavelength falling on it, is called black body, Such body emit radiation at fastest rate. The radiation emitted by blackbody is called black body radiation.

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Kirchoff's law : For a given wavelength the ratio of emissive power to absorptive power is same for all bodies at a given temperature and is equal to the emissive power of a black body or perfectly black body at that temperature.

$$\frac{e_\lambda}{a_\lambda} = E_\lambda$$

Stefan's law : According to this law energy radiated per unit time per unit area for any body is directly proportional to the fourth power of absolute temperature.

$$E \alpha T^4$$

$$E = \sigma T^4 \quad \rightarrow \text{For perfectly black body}$$

$$E = e \sigma T^4 \quad \rightarrow \text{For any body}$$

σ = Stefan's constant = 5.67×10^{-8} watt/m^2K^4

The net rate of flow of radiation per unit area = $\frac{1}{2}U_0C$

Stefan - Boltzmann law : Energy radiated per unit time per unit area is given by

$$E = e\sigma\left(T^4 - T_o^4\right)$$

where $T \rightarrow$ absolute temperature of surface that emits radiation

$T_o \rightarrow$ absolute temperature of external atomsphere or sorrounding

Let T be the temperature of any body that is slightly greater than temperature of sorrounding T_o such that

$$T - T_0 = t \quad \Rightarrow \quad T = t + T_0$$

$$E = e\sigma\left[(T_0 + t)^4 - T_0^4\right]$$

$$= e\sigma T_0^4\left[\left(1+\frac{t}{T_0}\right)^4 - 1\right] \qquad = 4\sigma\ T_0^3\ t = 4\sigma T_0^3\left(T - T_0\right)$$

$E\ \alpha\ T - T_0 \rightarrow$ Newton's law of cooling

It is limited to small temperature difference:

The most important application of B.E statistics is to investigate the equilibrium properties of black body radiation we consider a radiation cavity of volume V and temperature T.

The system can be looked upon from two practically identical but conceptually different point of view.

(1) As an assembly of harmonic oscillator with quantised energies

$$E_s = \left(n_s + \frac{1}{2}\right)\hbar\omega \qquad n_s = 0,\ 1,\ 2 \ldots$$

Where $\omega_s \rightarrow$ frequency of vibration

(2) As a gas of identical & indistinguishable quanta (photon)

The energy of photon corresponding to frequency ω_s of the radiation mode being $\hbar\omega_s$.

The distribution of photon in various quantum state of energy is given by

$$\langle n_s \rangle = f(\epsilon_s) = \frac{1}{\exp\left[\epsilon_s / k_B T\right] - 1} \quad (\mu = 0 \text{ for photon gas})$$

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The no. of vibrational modes of EmT wave in frequency range υ and $\upsilon + d\upsilon$ is given by

$$= 2 \times \frac{4\upsilon\pi}{h^3} p^2 dp = \frac{8\pi V \upsilon^2 d\upsilon}{c^3} \qquad \left| \quad p = \frac{h\upsilon}{c} \right.$$

Two factor is due to transverse nature i.e two direction tr to the direction of propagation

Average no. of photons between frequency range υ and $\upsilon + d\upsilon$

$$N(\upsilon)d\upsilon = \frac{2 \times V 4\pi p^2 dp}{h^3\left(e^{h\upsilon/k_B T} - 1\right)} = \frac{8\pi V \upsilon^2 d\upsilon}{c^3\left(e^{h\upsilon/k_B T - 1}\right)}$$

Total no. of photons in cavity of volume V

$$\frac{8\pi V}{c^3}\int \frac{\upsilon^2 d\upsilon}{e^{h\upsilon/k_BT}-1}$$

Let $\frac{h\upsilon}{k_BT} = x \quad \Rightarrow \quad d\upsilon = \frac{k_BT}{h}\,dx$

$$= \frac{8\pi V}{c^3}\int_0^\infty \frac{\left(\frac{k_BT}{h}\right)^3 x^2\,dx}{e^x - 1} \quad \Rightarrow \quad N \alpha T^3$$

The energy of photon in the range is $h\upsilon$ (radiant frequency in the range υ to $\upsilon + d\upsilon$)

$$U(\upsilon)d\upsilon = \frac{V\,8\pi\upsilon^3}{c^3\left(e^{h\upsilon/k_BT}-1\right)} h\upsilon \qquad \ldots (1)$$

Planck's formula for spectral energy distribution per unit Volume of black body radiation

Spectral energy density in the range λ to $\lambda + d\lambda$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{hc/\lambda k_BT}-1}$$

$c = \upsilon\lambda \Rightarrow \upsilon = \frac{c}{\lambda}$

$d\upsilon = -\frac{c}{\lambda^2}d\lambda$

(i) On longer wavelength (Smaller frequency side)

$\frac{hc}{\lambda} << k_BT$ or $h\upsilon < c\ k_BT$

$$u(\lambda)\,d\lambda = \frac{8\pi k_BT}{\lambda^4}\,d\lambda$$ Rayleigh Jean's law

(ii) on short wavelength(Longer frequency side)

$\frac{hc}{\lambda} >> k_BT$ $\quad h\upsilon >> k_BT$

$$u(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda k_BT}\,d\lambda$$ → Wein's law

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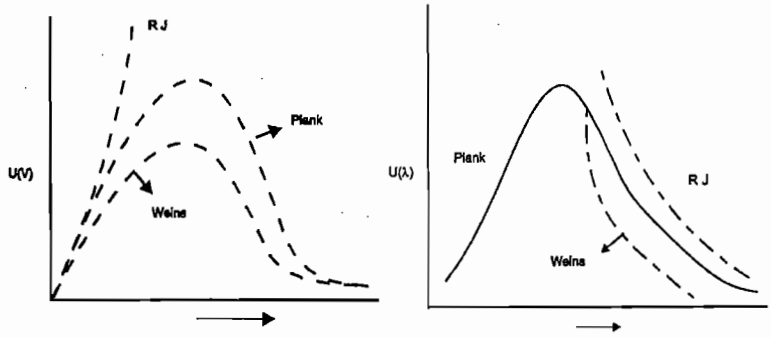

Deduction of Stefan's law from Planck's law :

At equilibrium total energy of the black body radiation inside an encloser of volume V (Black body radiation) at temperature T is given by

$$U(\upsilon)d\upsilon = \frac{8\pi V}{c^3}\frac{h\upsilon^3}{e^{h\upsilon/k_BT}-1}$$

Total energy

$$U(T) = \int_0^\infty U(\upsilon)d\upsilon = \int_0^\infty \frac{8\pi V h\upsilon^3}{c^3\left(e^{h\upsilon/k_BT}-1\right)}d\upsilon = \frac{8\pi Vh}{c^3}\int \frac{\upsilon^3 d\upsilon}{e^{h\upsilon/k_BT}-1}$$

$$\frac{h\upsilon}{k_BT} = x \quad \Rightarrow \quad d\upsilon = \frac{k_BT}{h}dx$$

Put $$U(T) = \frac{8\pi V}{(hc)^3}(k_BT)^4\int \frac{x^3}{e^x-1}dx$$

$$= \frac{8\pi V}{(hc)^3}(k_BT)^4 \times \frac{\pi^4}{15} = \frac{8}{15}\pi^5\frac{V(k_BT)^4}{(hc)^3}$$

$$\frac{U(T)}{V} = \frac{8}{15}\frac{\pi^5(k_BT)^4}{(hc)^3}$$

The net rate of flow of radiation per unit area

$$E = \frac{1}{4}\frac{U}{V}C = \frac{8}{10}\pi^5\frac{k_B^4T^4}{h^3c^2}$$

$$= \sigma T^4 \quad \text{where } \sigma = \frac{8}{60}\frac{\pi^5k_B^4}{h^3c^2}$$

By substituting the usual value $\sigma = 5.67\times10^{-8}\ w/m^2K^4$

Q. 79. Use Planck's formula to obtain expression for (a) Stefan's constant and (b) Wein's constant in terms of Planck's constant and Boltzmann's constant.

Ans. Using Planck's formula the total radiant energy in unit volume of an isothermal encloser is given by

$$U = \int_0^\infty E_\lambda d\lambda = 8\pi hc\int \frac{d\lambda}{\lambda^5\left(e^{\frac{hc}{\lambda k_BT}}-1\right)} \quad \text{(i)}$$

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But the total radiant energy in unit volume of an isothermal enclouser is also given by

$$U = AT^q \quad \text{... (ii)}$$

where A = constant T = absolute temperature of the encloser comparing eqn (i) and (ii) we have

$$AT^q = 8\pi hc\int_0^\infty \frac{d\lambda}{\lambda^5\left(e^{\frac{hc}{\lambda k_BT}}-1\right)}$$

Putting $X = \frac{hc}{\lambda k_BT}$ or $\lambda = \frac{hc}{\lambda k_BT} \Rightarrow d\lambda = \frac{-hc}{x^2k_BT}dx$

we have $AT^q = 8\pi hc \int_0^\infty \frac{-\frac{hc}{x^2 k_B T}}{\left(\frac{hc}{xk_BT}\right)^5 \left(e^x - 1\right)}$

$$= 8\pi hc \times \frac{hc}{k_BT} \times \left(\frac{k_BT}{hc}\right)^5 \int_0^\infty \frac{x^5}{x^2\left(e^x-1\right)} dx = \frac{8\pi k_B{}^4 T^4}{h^3c^3} \int \frac{x^3 dx}{e^x - 1}$$

$$\left[\int_0^\infty \frac{x^n dx}{e^x - 1} = \frac{\pi^{n+1}}{1.3.5..(2n-1)}\right]$$

$$AT^q = \frac{8\pi k_B{}^4 T^4}{h^3c^3} \times \frac{\pi^4}{1.3.5} = \frac{8\pi^5 k_B{}^4 T^4}{15h^3c^3} \Rightarrow A = \frac{8\pi^5 k_B{}^4}{15h^3c^3}$$

Since Stefan's ≠ constant (a) is given by

$$a = \frac{Ac}{4} = \frac{8\pi^5 k_B{}^4}{15 \times 4h^3c^3} \times c = \frac{2}{15} \frac{\pi^5 k_B{}^4}{h^3c^2} \rightarrow \text{Stefan's constant}$$

Weins constant : According to Wein's law Wein's constant is given by $b = \lambda_m T$ where λ_m is the wavelength for which the emitted energy is maximum and the expression for it

$$\lambda_m = \frac{hc}{9.965\, k_B T}, \quad \lambda_m T = \frac{hc}{9.965 k_B}$$

The weins constant $b\ (= \lambda_m T)$ is given by

$$\boxed{b = \frac{hc}{9.965\, k_B}}$$

Solar Constant: In the absence of atmosphere the energy of sun rays incident per unit area per minute perpendicular to the surface at average distance of earth from sun is called solar constant.

Let r is the radius of sun, R is the average distance of earth from sun. Consider sun as black body.

$$S = \frac{4\pi r^2 \times \sigma T^4}{4\pi R^2} \text{ or } \boxed{T^4 = \frac{S R^2}{\sigma r^2}}$$ where σ is Stefan's constant.

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Problems that appeared in GATE from this section :

Statement for Linked Answer Questions G-1 and G-2:

Consider a radiation cavity of volume *V* at temperature *T*.

G-1. The density of states at energy E of the quantized radiation (photons) is:

(a) $\frac{8\pi V}{h^3C^3}E^2$ **(b)** $\frac{8\pi V}{h^3C^3}E^{1/2}$ **(c)** $\frac{8\pi V}{h^3C^3}E$ **(d)** $\frac{8\pi V}{h^3C^3}E^{1/2}$

[GATE-2006]

Soln. It is well known that the nodes are formed at the end points of the string due to stationary vibrations and only certain discrete frequencies of vibrations are allowed. If l is the length of the string, the allowed wavelength are given by

$$\lambda = \frac{2l}{n} \quad \text{...(i)}$$

$n = 1, 2, 3, 4, ..., \infty$

The corresponding allowed frequencies are $\nu = \frac{c}{\lambda} = \frac{nc}{2l}$

$n = 1, 2, 3, 4, ..., \infty$ where, c is the speed of the waves.

In this case, the wave are confined to a three-dimensional space. Let each side of the cube be a. If we take the three intersecting edges of the cube as X, Y and Z-axis of a Cartesian coordinate system and cos α, cos β and cos γ as direction cosines of the direction of propagation of a particular wave, then the projections of the edges of the cube on the direction of propagation of the wave are a cos α a cos β and a cos γ respectively. In this case, the allowed wavelengths have to satisfy three conditions of the kind of equation (i), In which l is replaced by a cos α, a cos β and a cos γ respectively. Thus, an allowed wavelength λ must satisfy

$$\lambda = \frac{2a\cos\alpha}{n_1}, \quad \lambda = \frac{2a\cos\beta}{n_2} \text{ and } \lambda = \frac{2a\cos\gamma}{n_3}$$

where, n_1, n_2 and n_3 are positive integers.

Using, trignometric condition of direction cosines,

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1 \quad \text{...(ii)}$$

Substituting values of cos α, cos β and cos γ in equation (ii), we have

$$\frac{n_1^2\lambda^2}{4a^2} + \frac{n_2^2\lambda^2}{4a^2} + \frac{n_3^2\lambda^2}{4a^2} = 1 \quad \textbf{or} \quad n_1^2 + n_2^2 + n_3^2 = \frac{4a^2}{\lambda^2} = \left(\frac{2a}{\lambda}\right)^2 \quad \text{...(iii)}$$

As $\lambda = \frac{c}{\nu}$, we have $n_1^2 + n_2^2 + n_3^2 = \left(\frac{2a\nu}{c}\right)^2$ ...(iv)

The number of modes of vibbrations within the frequency interval ν and $\nu + d\nu$ can be found with the help of equation (iv).

For simplicity, let us first count the modes of vibration in an analogous two-dimensional problem. The two-dimensional equation will be

$$n_1^2 + n_2^2 = \left(\frac{2a\nu}{c}\right)^2 \quad \text{...(v)}$$

This represents a circle of radius $\left(\frac{2a\nu}{c}\right)$

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Thus, the number of modes of vibration within frequency interval ν and $\nu + d\nu$ is equal to the area in the positive quadrant lying between two circles of radii $\frac{2a\nu}{c}$ and $\frac{2a(\nu + d\nu)}{c}$.

$$\text{Area} = \frac{1}{4}\pi\left[\left\{\frac{2a(\nu + d\nu)}{c}\right\}^2 - \left(\frac{2a\nu}{c}\right)^2\right] = \frac{\pi}{4} \times \frac{8a^2\nu d\nu}{c^2} = \frac{2\pi a^2\nu}{c^2} d\nu$$

The number of modes of vibration within frequency range ν and $\nu + d\nu$ is now equal to the volume of the constant $(1/8)^{th}$ of the spherical shells with radii $\frac{2a\nu}{c}$ and $\frac{2a(\nu + d\nu)}{c}$ i.e.,

$$= \frac{1}{8}\left[\frac{4}{3}\pi\left(\frac{2a\nu}{c}\right)^3 - \frac{4}{3}\pi\left\{\frac{2a(\nu + d\nu)}{c}\right\}^3\right]$$

$$= \frac{1}{8} \times \frac{4}{3}\pi \times \frac{8a^3}{c^3}\left[\nu^3 - \nu^3 + 3\nu^2 d\nu\right]$$

$$= \frac{4\pi a^3 \nu^2}{c^3} d\nu$$

But $a^3 = V =$ volume of the cube

Therefore, the modes of vibration inside cubical encloser with frequency range ν and $\nu + d\nu$ will be

$$= \frac{4\pi V \nu^2 d\nu}{c^3}$$

$\therefore$ Number of modes of vibration per unit volume with frequency range ν and $\nu + d\nu$ will be

$$= \frac{4\pi \nu^2 d\nu}{c^3}$$

Since, the black body radiation travel with velocity of light c and are transversed in character and hence, modes of vibrations are double as that for longitudinal waves.

Therefore, for black body radiation or electromagnetic waves, the number of modes of vibration per until volume within frequency range ν and $\nu + d\nu$ will be

$$= 2 \times \frac{4\pi \nu^2 d\nu}{c^3} = \frac{8\pi \nu^2 d\nu}{c^3} \quad \text{...(vi)}$$

$\therefore$ $\nu = E/H$, hence, it is clear from equation (vi) the number of modes of vibration or density of states is $8\pi V E^2/h^2c^3$.

Hence correct option is (a).

G-2. The average number of photons in equilibrium inside the cavity is proprotional to
(a) T (b) T^2 (c) T^3 (d) T^4

[GATE-2006]

Soln. Average number of photons $\propto T^3$.

Hence correct option is (c).

G-3. Consider black body radiation in a cavity maintained at 2000 K. If the volume of the cavity is reversibly and adiabatically increased from 10 cm^3 to 640 cm^3, the temperature of the cavity changes to
(a) 800 K (b) 700 K (c) 600 K (d) 500 K

[GATE-2004]

Soln. According to Wien's displacement law, $\lambda_m T =$ constant.

$\therefore$ $T_1(V_1)^{1/3} = T_2(V_2)^{1/3}$

Given, $T_1 = 2000\ K, V_1 = 10\ cm^3$

$V_2 = 640\ cm^3$

$T_2 = ?$

Hence, $2000 \times (10)^{1/3} = (640)^{1/3}.T_2$ **or** $T_2 = 2000\left(\frac{10}{640}\right)^{1/3} = \frac{2000}{4} = 500\ K.$

Hence correct option is (c).

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G-4. The temperature of a cavity of fixed volume is doubled. Which of the following is true for the black-body radiation inside the cavity? [GATE-2003]

(a) Its energy and the number of photons both increase 8 times.
(b) Its energy increases 8 times and the number of photons increase 16 times.
(c) Its energy increases 16 times and the number of photons increases 8 times.
(d) Its energy and the number of photons both increases 16 times.

Soln. For black body radiation inside a cavity, we have $E \propto T^4$ (provided volume is constant)

$\therefore$ If temperature is doubled, the energy will increase by 16 times.

Also, since for a black body radiation, the radiation is in equilibrium with matter.

$\therefore$ Energy of each photon $\approx k_B T$

$\Rightarrow$ Energy of each photon after temperature is doubled $= 2k_B T$

$$\text{Now, no. of photons} = \frac{\text{Total energy}}{\text{Energy of each photons}} = \frac{16 \times \text{initial energy of the cavity}}{2 \times \text{initial energy of each photon}}$$

$= 8 \times$ initial no. of photons.

Therefore, no. of photons increases by 8 times.

Hence correct option is (c).

G-5. A system of N non-interacting and distinguishable particles of spin 1 is in thermodynamic equilibrium. The entropy of the system is:

(a) $2k_B \ln N$ **(b)** $3k_B \ln N$ **(c)** $Nk_B \ln 2$ **(d)** $Nk_B \ln 3$

[GATE-2011]

Soln. Total number of microstates for a particle with spin $S = 2S + 1$.

$\therefore$ Total number of accessible microtates for N particles with spin $S \equiv (2S+1)^N = \Omega$

Now, entropy $\equiv k_B \ell n\, \Omega = k_B \ell n \left[(2S+1)^N\right]$

Putting $S = 1$

$\Rightarrow$ Entropy $= k_B \ell n \left[(2+1)^N\right] = Nk_B \ell n 3$

Hence correct option is (d).

G-6. If Planck's constant were zero, then the total energy contained in a box filled with radiation of all frequencies at temperature T would be (k is the Boltzmann constant and T is non-zero)

(a) zero (b) infinite (c) 3/2 $k_B T$ (d) $k_B T$ [GATE-2013]

Soln. At equilibrium, the total energy of the black-body radiation inside an enclosure of volume V and at temperature T, is given by $U(T) = \dfrac{8\pi hV}{c^3} \int_0^{\infty} \dfrac{\nu^3\, d\nu}{e^{h\nu/k_B T} - 1}$

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Now, if we take the limit h tending to zero (classical limit), then we have

$$\lim_{h\to 0} U(T) = \lim_{h\to 0} \frac{8\pi hV}{c^3} \int_0^{\infty} \frac{\nu^3\, d\nu}{e^{h\nu/k_B T} - 1} = \lim_{h\to 0} \frac{8\pi V}{c^3} \int_0^{\infty} \frac{h\nu^3}{e^{h\nu/k_B T} - 1}\, d\nu$$

$$= \frac{8\pi V}{c^3} \int_0^{\infty} \frac{h\nu^3\, d\nu}{1 + \dfrac{h\nu}{k_B T} - 1} \qquad (\because\ h \to 0, \text{ neglecting higher order terms of } \frac{h\nu}{k_B T})$$

$$= \frac{8\pi V}{c^3} \int_0^{\infty} \frac{h\nu^3}{h\nu} k_B T\, d\nu = \frac{8\pi V k_B T}{c^3} \int_0^{\infty} \nu^2\, d\nu$$

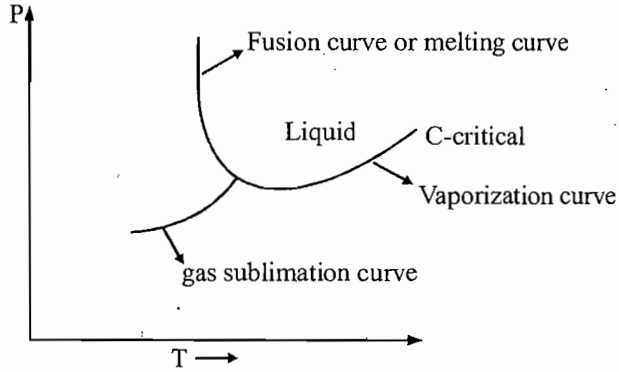
from the above result it is clear that the total energy will turn out to be infinite.

Hence correct option is (b).

PHASE TRANSITION

Phase transition : We consider a system whose phases are in equilibrium. In slight variation of external condⁿ (T,P) results a certain amount of the substance passing from one phase to another and this phenomena is called phase transition

Phase diagram :



1. **Triple point :** The point (unique temperature and pressure) at which all three phases can co-exist in equilibrium with each other is called triple point.

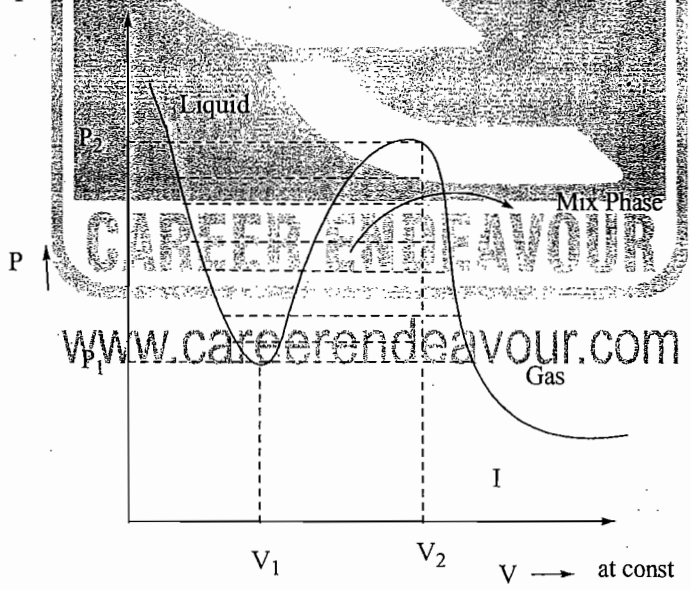
or

The point at which three curves intersect is known as triple point.

Critical point :

The point at which liquid vapour equilibrium lying ends. Above the critical point there is no further phase transition. Since there exist only one phase (gas or liquid)

In the shaded region mixture of two phases can co-exist along the horizontal line. At a given temperature T for $P < P_1$ there must be unique value of V for each value of P. Then there exist a well defined single phase.



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$\frac{\partial P}{\partial V}$ for region I is small. So isothermal compressibility $-\frac{1}{V}\frac{\partial V}{\partial P}$ is large as in case of gaseous phase

At a given temperature for $P > P_2$ there are also unique value of V for each value of P. For this part $\frac{\partial P}{\partial V}$ is large,

So compressibility is small as in the case of liquid phase.

In the region $P_1 < P < P_2$ there is no unique value of V for each value of P. In this region there is a mixture of two phases that co-exist along the horizontal line.

First order phase transition :

We shall consider the cond^{n} of equilibrium of two phases. Gibb's free energy is a function of (T,P,N) i.e $G = G(T,P,N)$

At constant T and P $\quad G = N\,g(T,P)$ so $\mu = \dfrac{F}{N} = g(T,P)$

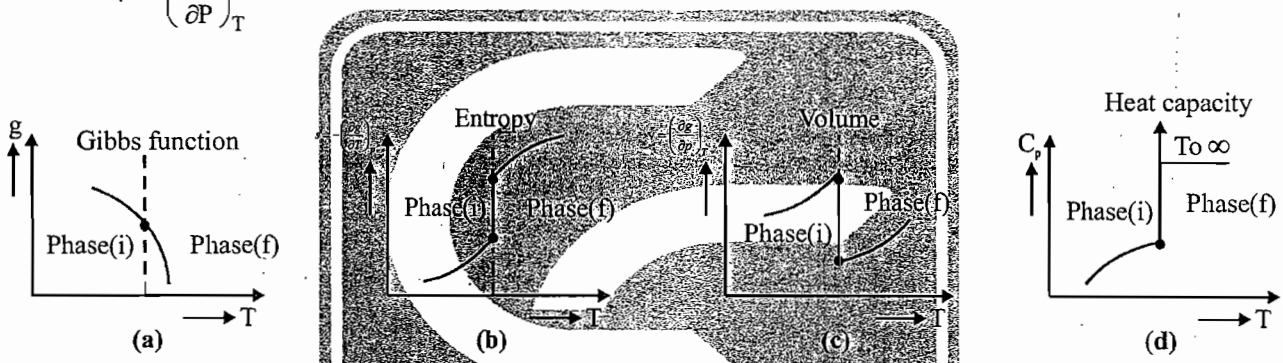
$$G = A + PV = U - TS + PV$$

$$Nd\mu + \mu dN = TdS - PdV - TdS - SdT + PdV + VdP + \mu dN$$

$$Nd\mu = -SdT + VdP \qquad \Rightarrow d\mu = \frac{-S}{N}dT + \frac{V}{N}dP$$

$$S = -\left(\frac{\partial \mu}{\partial T}\right)_P \; N = -\left(\frac{\partial G}{\partial T}\right)_P \qquad \Rightarrow \quad S = -\left(\frac{\partial G}{\partial T}\right)_P$$

$$V = \left(\frac{\partial G}{\partial P}\right)_T$$



First order phase transition can be characterised by either of following statement

(i) First order derivative of free energy change discontinously or first order derivative of free energy are discontinuous at transition point.

Ex- entropy, Volume, magnetisation, density are discontinuous

The density changes discontinuously at transition point.

Example:

1. Vapour liquid transition away from the critical point (Along vapourisation curve)

(ii). Conversion of water into water vapour.

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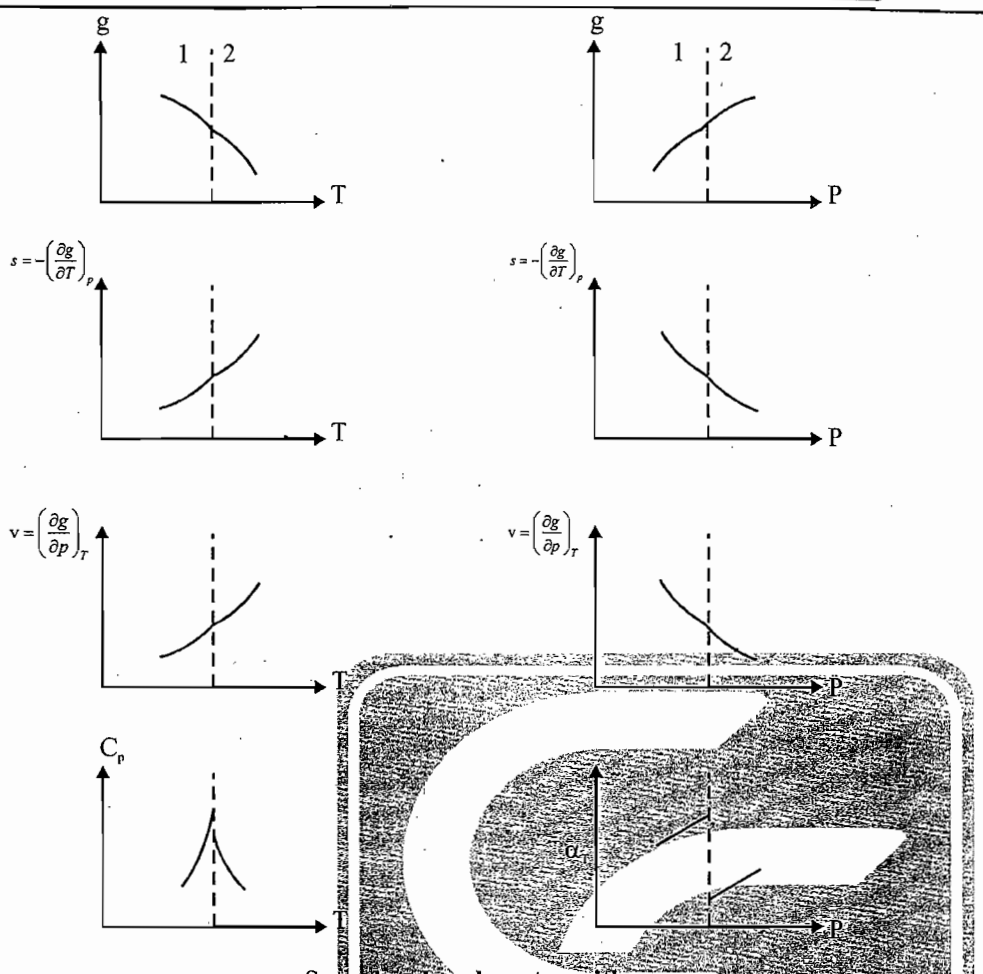
Second order phase transition : If the 1st order deriviative of free energy are continuous and 2nd order are discontinuous at transition point then the phase transition is called 2nd order phase transition or continuous phase transition.

The 2nd order phase transition is continuous in the sense that the state of the body changes continuously but discontinuous in the sense that the symmetry of the body changes discontinuously (specific heat, susceptibility

$\chi = \dfrac{M}{H} = \dfrac{\partial M}{\partial H}$ compressibility $\dfrac{-1}{V}\left(\dfrac{\partial V}{\partial P}\right)$ are discontinuous.



Second-order phase transitions

Ex → 1. Transition of He-I to He-II for common isotope $_2He^4$
2. Transition from non-ferro magnetic to Ferromagnetic
3. Ferromagnetic to paramagnetic
4. Transition from super conducting to conducting state & vice-versa
5. Phase transition of liquid gas at critical points

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Q. 80. The vapour pressure P (in mm of Hg) of a solid at temperature T expressed by $\ell n\, P = 23 - \frac{3863}{T}$ and that of its liquid phase by $\ell n\, P = 19 - \frac{3063}{T}$. For triple point of the material temp is

(a) 200 **(b) 195** **(c) 300** **(d) 260**

Ans. For triple point

$$23 - \frac{3863}{T} = 19 - \frac{3063}{T}$$

$$\frac{3863}{T} - \frac{3063}{T} = 23 - 19$$

$$800 = 4T \quad \Rightarrow \quad T = 200$$

Q. 81. Show that with the increase in pressure, boiling point of liquid increases and the melting point of substances which contract on melting decreases.

Ans. In case of boiling V_2 represents the specific volume of the vapour and V_1 that of the liquid phase of the substance

For all substances the specific volume in vapour phase is always larger than that in the liquid phase

Thus if the liquid phase is changed into vapour phase $V_2 - V_1$ is always +ve it follows from the Clapeyron's equation

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

will be + ve since L & T are essentially +ve quantities Hence in case of the boiling point of a liquid an increase in pressure (dP > 0) will give a + ve value of dT.

It means the boiling points is raised by an increase in pressure. It has been found true for all liquids.

Change in melting point : In case of melting V_1 & V_2 represents the specific volumes of the substances in the solid & liquid phase respectively.

Now with the increase in pressure dT will be +ve if $V_2 - V_1$ is +ve (if $V_2 > V_1$) and dT will be –Ve if $V_2 - V_1$ is –Ve (if $V_2 < V_1$).

Thus the substances which expands on melting $\frac{dP}{dT}$ is +ve i.e. the melting point of substance which expands on melting increases with increase of pressure.

On the other hand if $V_2 < V_1$ i.e for substances which contracts on melting $\frac{dP}{dT}$ is $-Ve$ & therefore melting point of substances which contracts on melting decreases with increase of pressure.

Problems that appeared in GATE from this section :

G-1. In a first order phase transition, at the transition temperature, specific heat of the system
(a) diverges and its entropy remains the same
(b) diverges and its entropy has finite discontinuity
(c) remains unchanged and its entropy has finite discontinuity
(d) has finite discontinuity and its entropy diverges

[GATE-2011]

Soln. The key points are:
(i) specific heat diverges for both 1st and 2nd order phase transitions.
(ii) The entropy has a finite discontinuity only for 1st order phase transition is continuous for 2nd order phase transition.

Keeping the above key points in mind, we can see that correct answer is (b).
Hence, the correct option is (b).

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G-2. Identity which one is a first order phase transition?
(a) A liquid to gas transition at its critical temperature
(b) A liquid to gas transition close to its triple point
(c) A paramagnetic to ferromagnetic transition in the absence of a magnetic field
(d) A metal to superconductor transition in the absence of a magnetic field

[GATE-2009]

Soln. Clearly option (c) and (d) are not first order phase transition as it involves symmetry variation. So now the confusion can arise only with option (a) and (b). Inorder to avoid that confusion, the key point is the definition of critical point. Beyond the critical point, no phase transition is possible, therefore it cannot be the right answer.
Hence, the correct option is (b).

G-3. Which one of the following is a first order phase transition?
(a) Vaporization of a liquid at its boiling point
(b) Ferromagnetic to paramagnetic
(c) Normal liqiuid He to superfluid He
(d) Superconducting to normal state

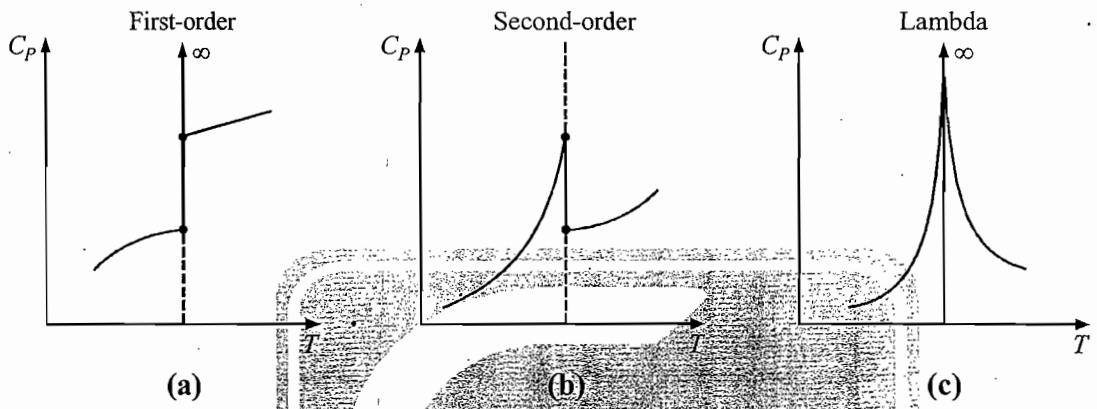
[GATE-2004]

Soln. Vaporization of a liquid at its boiling point, in which only phase is changed, is the first order phase transition but in other three options, the structure of material is changed, so these are second order phase transition.
Hence correct option is (a).

G-4. A second order phase transition is one in which
(a) the plot of entropy as a function of temperature shows a discontinuity
(b) the plot of volume heat as a function of temperature shows a discontinuity
(c) the plot of volume as a function of pressure shows a discontinuity
(d) the plot of comprehensility as a function of temperature is continuous

[GATE-2003]

Soln.



(a) **(b)** **(c)**

Distinguish characteristics among the three types of phase transitions: (a) first order; (b) second order; (c) lambda.
Hence correct option is (b).

G-5. The vapour pressure p (in mm of Hg) of a solid, at temperature T, is expressed by $\ell n\ p = 23 - 3863/T$ and that of its liquid phase by $\ell n\ p = 19 - 3063/T$. The triple point (in Kelvin) of the material is:
(a) 185 **(b) 190** **(c) 195** **(d) 200**

[GATE-2007]

Soln. At triple point the vapour pressure of solid and liquid phases are equal.

$$\text{Hence, } 23 - \frac{3863}{T} = 19 - \frac{3063}{T}$$

$$\Rightarrow 4 - \frac{3863}{T} = -\frac{3063}{T}$$

$$\Rightarrow 4T - 3863 = -3063$$

$$\Rightarrow 4T = 3863 - 3063$$

$$\text{or } 4T = 800$$

$$T = 200\ \text{K}$$

Hence correct option is (d).

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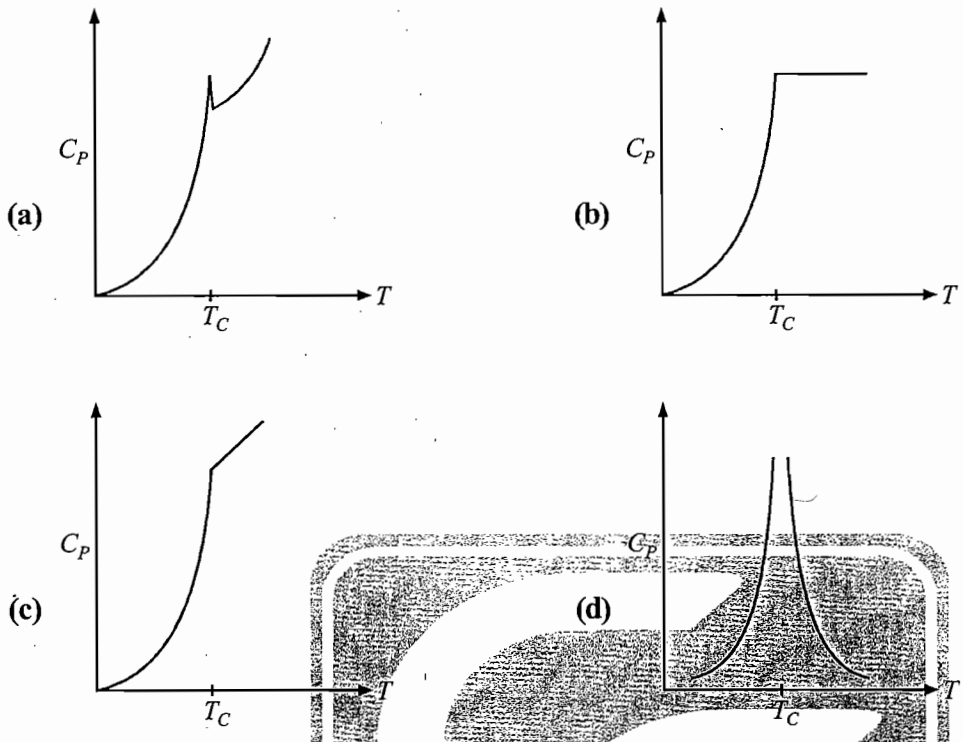
G-6. The plot of specific heat versus temperature across the superconducting transition temperature (T_c) is most appropriately represented by



[GATE-2014]

Soln. Phase transition for superconducting state is a second order phase transition. For second order phase transition the C_p has a finite discontinuity at the transition temperature.

Hence correct option is (a).

G-7. Across a first order phase transition, the free energy is

(a) proportional to the temperature

(b) a discontinuous function of the temperature

(c) a continuous function of the temperature but its first derivative is discontinuous

(d) such that the first derivative with respect to temperature is continuous

[GATE-2013]

Soln.

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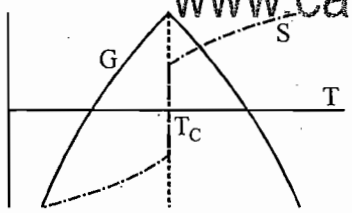

Figure : Schematic diagram for the Gibbs free energy and the entropy in a first order phase transition.

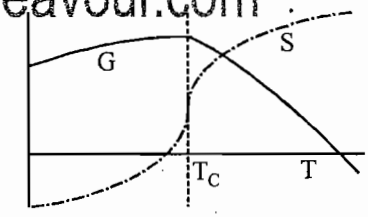

Figure : Schematic diagram for the Gibbs free energy and the entropy in a continuous phase transition.

From the above we can see that for first order transition the Gibbs free energy is itself continuous function of temperature but at the transition temperature there is a discontinuity in its first derivative.

Hence correct option is (c).

Appendix-i : The Ising Model

The ising model is in important statistical model which is used to understand the magnetic state of a paramagnetic system by considering the individual spins states that comprise the system. It is assumed that the paramagnetic system is formed by individual spins arranged next to each other. By considering the interaction between these spins we can know about the magnetization state of the paramagnetic system. For simplicity we assume that there is only nearest neighbour interaction between permanent dipole. Under this condition the Hamiltonian of the system can be written as

$$H_i = -\mu_i\beta \text{ (where } \mu \text{ is the magnetic moment of the spin)}$$

$$H = -\sum_{i=1}^{N}\mu_i\beta - J_1\sum_{i=1}^{N}S_i\,S_j + 1 - J_2\sum_{i,j}^{N}S_i\,S_j\,S_k .... + ...$$

This is the energy interaction term of three body system

put fund $Q_N(V,T) = \sum_s e^{-\beta H}$

$A = -kT\ln\left(Q_N(V,T)\right)$

In one dimension number of nearest neighbour = 2
In two dimension number of nearest neighbour = 4
In three dimension number of nearest neighbour = 6
In d dimension number of nearest neighbour = 2d

Ising Model in one dimensional:

Consider M dipole if this system is in external magnetic field H.

$$\mu_z = \frac{2q}{2m}S_z,\ S_z = m_s\hbar\ ,\ \mu_z = \frac{2q\,m_s\hbar}{2m} \quad ... (1)$$

$$H = -B\sum_{|z|}^{N}\mu_z$$

$$\boxed{H = -A\,B\sum_{i=1}^{N}\sigma_i - J\sum_{i=1}^{N-1}\sigma_i - \sigma_{i+1}} \qquad \boxed{H = -k\sum_{i=1}^{N}\sigma_i - J\sum_{i=1}^{N-1}\sigma_i - \sigma_{i+1}}$$

$$Q_N(V,T) = \sum_{\{\sigma_i\}}e^{-\beta H}\ ;\ Q_N(V,T) = \sum_{\{\sigma_i\}}e^{+\beta\left[K\sum_{i=1}^{N}\sigma_i - J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}\right]}$$

In the absence of magnetic field K=AB
1st term is zero $A\times 0 = 0$

$$Q_N(V,T) = \sum_{\{\sigma_i\}}e^{+\beta J\sum_{i=1}^{N-1}\sigma_i\sigma_{i+1}}$$

Suppose we consider N =3 $\boxed{\left[\sigma_i \pm 1\left\{\begin{matrix}\uparrow & \uparrow\\ \downarrow & \downarrow\end{matrix}\right\}(1)\left\{(-)\begin{matrix}\uparrow & \downarrow\\ \downarrow & \uparrow\end{matrix}\right\}\right]}$; $Q_N(V,T) = \sum_{\sigma_1}\sum_{\sigma_2}\sum_{\sigma_3}e^{\beta J\sum_{i=1}^{2}\sigma_i\,\sigma_{i+1}}$

$$\boxed{Q_N(V,T) = \sum_{\sigma_1}\sum_{\sigma_2}\sum_{\sigma_3}e^{\beta J(\sigma_1\,\sigma_2 + \sigma_2\,\sigma_3)}}$$

There are only two values for each summation (+1 and −1)

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$$Q_N(V,T)=\sum_{\sigma_1}\sum_{\sigma_2}\left[e^{\left[\beta J(\sigma_1\sigma_2+\sigma_2(+1)\right]}+e^{\beta J\left[\sigma_1\sigma_2+\sigma_2(-1)\right]}\right]$$

$$Q_N(V,T)=\sum_{\sigma_1}\left[e^{\left[\beta J\sigma_1(+1)+(+1)+(+1)\right]}+e^{\beta J\left[\sigma_1(+1)+(+1)(-1)\right]}\right]\ e^{\beta J\left[J_1(-1)+(-1)(+1)\right]}+e^{\beta J\left[\sigma_1(-1)+(-1)(-1)\right]}$$

$$\Rightarrow\ \exp\left[\beta J(+1)\ (+1)+(+1)(+1)\right]+\exp\left[\beta J(+1)\ (+1)+(+1)(-1)\right]$$

$$+\exp\beta J\left[(+1)\ (-1)+(-1)(+1)\right]+\exp\beta J\left[(+1)\ (-1)+(-1)(-1)\right]$$

$$+\exp\left[\beta J(-1)\ (+1)+(+1)(+1)\right]+\exp\left[\beta J(-1)\ (+1)+(+1)(-1)\right]$$

$$+\exp\left[\beta J(-1)\ (+1)+(+1)(+1)\right]+\exp\left[\beta J(-1)\ (+1)+(-1)(-1)\right]$$

$$=e^{2\beta J}+e^{0}+e^{-2\beta J},+e^{0}+e^{-2\beta J}+e^{0}+e^{2\beta J}=2\left[e^{2\beta J}+e^{-2\beta J}+2\right]=2\left(e^{\beta J}+e^{\beta J}\right)^2=2\left[2\cos\hbar(\beta J)\right]^2$$

$$Q_3(V,T)=2^2\times2(\cos\hbar\,\beta J)^{3-1}=2^3\left[\cos\hbar\,\beta J\right]^{3-1}$$

Similarly for two particles

$$H=Q_N(V,T)_2\sum_{\sigma_1}\sum_{\sigma_2}e^{\beta J\sum_{i=1}^{2}\sigma_i\sigma_{i+1}}=\sum_{\sigma_1\sigma_2}\left[e^{\beta J[\sigma_1\sigma_2]}\right]=e^{\beta J\left[\sigma_1(+1)\right]}+e^{\beta J\sigma_1(-1)}$$

$$=e^{\beta J(-1)(-1)}+e^{\beta J(-1)(+1)}+e^{\beta J(-1)(-1)}+e^{\beta J(-1)(-1)}=2\left[e^{\beta J}+e^{-\beta J}\right]$$

$$Q_2(V,T)=2^2\left[\cos\hbar\,\beta J\right]$$

For N dipole

$$\boxed{Q_N(V,T)=2^N(\cos\hbar\beta J)^{N-1}}$$

$$A=-k_BT\ell n\,Q_N(V,T)=-k_BT\ell n\,2^N\left[\cos\hbar(13J)^{N-1}\right]$$

$$=-k_BT\left[N\ell n2+(N-1)\ell n\cos\hbar(\beta J)\right]=-k_BT\left[N\ell n\,2-(N-1)kT\ell n\cos\hbar(\beta J)\right]$$

$$A=-Nk_BT\left[\ell n\,2+\left(\frac{N-1}{N}\right)\ell n\cos\hbar(\beta J)\right]\ \text{if}\ N\to\infty$$

$$A=-Nk_BT\left[\ell n\,2+\ell n\cos(\hbar\beta J)\right]$$

$$\boxed{A=-Nk_BT\ell n\left[2\cos\hbar\beta J\right]}\quad\ldots(i)$$

$$S=-\frac{\partial A}{\partial T}\qquad[\beta\text{ is also the function of T}]$$

we can calculate all the properties with the help of value of A.

if $B\neq0\Rightarrow$ $\boxed{Q_N(V,T)=2^N(\cos\hbar\,\beta J)^{N-1}(2\cos\hbar\,\beta\varepsilon)^N}$

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Q. 82. Consider a system of two Ising spins S_1 and S_2 taking values ± 1 with interaction energy given by $\in = -JS_1S_2$, when it is in thermal equilibrium at temperature T for larger T_1 the average energy of the system varies as $\frac{C}{k_BT}$, find the value of *C*.

Soln. $\in_1 = -J(g_1 = 2),\ \in_2 = +J(g_2 = 2)$

$$\langle E \rangle = \frac{\sum_r g_r E_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}} = \frac{2(-J)e^{\beta J} + 2(J)e^{-\beta J}}{2e^{\beta J} + 2e^{-\beta J}} = \frac{-J[e^{\beta J} - e^{-\beta J}]}{e^{\beta J} + e^{-\beta J}}$$

For large temperature β is very small

$$\langle E \rangle = \frac{-J[1 + \beta J - 1 + \beta J]}{[1 + \beta J + 1 - \beta J]}$$

(neglecting higher order terms)

$$\langle E \rangle = -J\frac{2\beta J}{2} = -\beta J^2 = -\frac{J^2}{k_BT}$$

Comparing this with $\frac{C}{k_BT}$

$\Rightarrow C = -J^2$

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Appendix-ii : Summary of key points

1. Thermodynamic Limit

   If $N \to \infty \quad V \to \infty$

   Then particle density $n = \frac{N}{V}$ = fixed at a preassigned value

2. Extensive property $\to$ N, V, E, S, A
   Intensive property $\to$ P, T, μ

3. Relation between thermodynamics & statistical mechanics or Boltzmann entropy probability relation

$$S = k_B \log \Omega = -k_B \sum_r P_r \ell n P_r$$

   Where $\Omega \to$ number of microstate for a given macrostate.

4. The probability in which r particle in state A and N-R particle in state B is $= \frac{N!}{r!(N-r)!} (P)^r (1-P)^{N-r}$

5. The no. of microstate for N no. of spin S particle is $= (2S+1)^N$

6. The probability of getting a microstate in which there are r particle out of N spin $\frac{1}{2}$ particle in spin up state

$= {}^{N}C_r \times \frac{1}{2N}$.

7. The entropy for classical ideal gas $S = Nk_B \ell n \left(\frac{V}{h^3}\right)\left(\frac{4\pi mE}{3N}\right)^{\frac{3}{2}} + \frac{3}{2} Nk_B$

   or $S = Nk_B \ell n V + \frac{3}{2} Nk_B \left[1 + \ell n \frac{2\pi m T k_B}{h^2}\right]$

8. Sackur tetrode eqn (The eqn that satisfy entropy is an extensive property)

$$S = Nk_B \ell n V + \frac{3}{2} Nk_B \left[\frac{5}{3} + \ell n \left(\frac{2\pi m k_B T}{h^2}\right)\right]$$

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9. Valume of phase Cell = h^f
   Dimension of phase space = 2Nf
   f $\to$ degree of freedom N $\to$ no. of particles

$$\text{No. of microstate in phse space} = \frac{\text{Total Volume of phase space allowed to the system}}{\text{Volume of phase cell}}$$

10. $P_r = \frac{g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}$

11. Partition function for Q.M system (energy discontinuous)

$$Q_N(V,T) = \sum_r g_r e^{-\beta E_r}$$

12. Partition function for classical distinguishable system

$$Q_N(V,T) = \frac{1}{h^{3N}} \int e^{-\beta E_r} d^3p\, d^3q$$

13. Partition function for classical indistinguishable system

$$Q_N(V,T) = \frac{1}{N!h^{3N}} \int e^{-\beta E_r} d^3p\, d^3q$$

14. $Q_N(V,T) = [Q_1(V,T)]^N \rightarrow$ for distinguishable

$$= \frac{1}{N!}[Q_1(V,T)]^N \rightarrow \text{for indistinguishable.}$$

15. Average energy or internal energy

$$U = \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = -\frac{\partial}{\partial \beta} \ell n\ Q_N(V,T)$$

16. $A = U - TS \Rightarrow dA = dU - TdS - SdT \Rightarrow dA = TdS - PdV + \mu dN - TdS - SdT$

$$dA = \mu dN - PdV - SdT$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} \qquad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

17. Internal energy or average energy

$$U = -T^2 \frac{\partial}{\partial T}\left(\frac{A}{T}\right)_{N,V} = \frac{\partial}{\partial \beta}\left(\frac{A}{kT}\right)_{N,V} = -\frac{\partial}{\partial \beta} \ell n\ Q_N(V,T)$$

18. Helmholtz free energy

$$A = -k_B T \ell n\, Q_N(V,T)$$

19. Specific heat

$$C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_N$$

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Appendix-iii : Miscellaneous solved examples

Q. 83. Obtain an expression for the specific heat capacity of a solid on the basis of Einstein's theory. How far do the results from these theories agree's with experimental data?

Ans. Einstein in 1907 applied quantum principle to the thermal vibration of atoms in solids.

He consider a solid of N_A atom (per kg mole of substance) to behave as $3\ N_A$ independent harmonic ascillators each of frequency υ

Quantum theory assumes that atoms are again identical independent harmonic ascillators all of which vibrate independently with the same natural frequency but have discrete energy vaues. These discrete energy values are given by Planck's formula

$$E = nh\upsilon = n\hbar\omega \qquad \ldots (i)$$

If dN oscillators have energies lying between E & E + dE then the mean energy of the atomic oscillator is given by

$$\bar{E} = \frac{\Sigma E dN}{\Sigma dN} \qquad \ldots (1)$$

From statistical mechanics one knows that the number of atomic oscillators dN having energies lying between E & E + dE at temperature T is proportional to e^{-E/K_BT}

$$\bar{E} = \sum_{n=0}^{\infty} nh\upsilon\, e^{-nh\upsilon/k_BT} \Big/ \sum e^{-nh\upsilon/k_BT}$$

$$= \frac{h\upsilon\left[e^{-h\upsilon/k_BT} + 2e^{-2h\upsilon/k_BT} + 3e^{-3h\upsilon/k_BT} + \ldots \infty \text{ terms}\right]}{1 + e^{-h\upsilon/k_BT} + e^{-2h\upsilon/k_BT} + e^{-3h\upsilon/k_BT} + \ldots \infty \text{ terms}}$$

Put $X = -h\upsilon / k_BT$

$$\bar{E} = \frac{h\upsilon\left(e^{x} + 2e^{2x} + 3e^{3x} + \ldots\right)}{\left(1 + e^{x} + e^{2x} + \ldots\ldots\right)}$$

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$$= h\upsilon\left[\frac{d}{dx}\log\left(1 + e^{x} + e^{2x} + \ldots\ldots \infty \text{ term}\right)\right]$$

$$= h\upsilon\left[\frac{d}{dx}\log\frac{1}{1-e^{x}}\right] = h\upsilon\left[\frac{d}{dx}[\log 1 - \log(1-e^{x})\right]$$

$$= h\upsilon\left[-\frac{(-e^{x})}{1-e^{x}}\right] = h\upsilon\frac{e^{x}}{1-e^{x}} = h\upsilon\frac{1}{e^{-x}(1-e^{x})}$$

$$= h\upsilon\frac{1}{e^{-x}-1} = h\upsilon\frac{1}{\left(e^{\frac{h\upsilon}{k_BT}} - 1\right)} \qquad \ldots (iii)$$

The total internal energy of a kg mole of a solid therefore becomes

$$U = 3N_A\bar{E} = \frac{3N_A h\upsilon}{h\upsilon}$$

and the molar specific heat is $C_V = \frac{dU}{dT} = \frac{-3N_A h\upsilon e^{\frac{h\upsilon}{k_BT}}\left(-\frac{h\upsilon}{k_BT^2}\right)}{\left(e^{\frac{h\upsilon}{k_BT}}-1\right)^2}$

$$C_V = \frac{3N_A k\left(\frac{h\upsilon}{k_BT}\right)^2 e^{\frac{h\upsilon}{k_BT}}}{\left(e^{\frac{h\upsilon}{k_BT}}-1\right)^2} = 3R\left(\frac{h\upsilon}{k_BT}\right)^2 \frac{e^{\frac{h\upsilon}{k_BT}}}{\left(e^{\frac{h\upsilon}{k_BT}}-1\right)^2} \quad \text{... (iv)}$$

Case - 1 $\rightarrow$ At high temperature $h\upsilon < k_BT$

Let $x = \frac{h\upsilon}{k_BT} \Rightarrow$ eqn (iii) becomes

$$\bar{E} = \frac{h\upsilon}{1+x-1} = \frac{h\upsilon}{x} = \frac{h\upsilon}{h\upsilon} k_BT = k_BT$$

$$u = 3N_A \bar{E} = 3N_A k_BT = 3RT$$

$$\boxed{C_V = \frac{dU}{dT} = 3R}$$

i.e for large values of T, the expression reduces to classical expression

Case-II: At low temperature $h\upsilon >> k_BT$ and hence $e^{\frac{h\upsilon}{k_BT}} >> 1$ therefore

$$\bar{E} = \frac{h\upsilon}{e^{\frac{h\upsilon}{k_BT}}}$$

Thus at low temperature the total energy of a kg mole of a solid is given by

$$U = 3N_A h\upsilon\, e^{-\frac{h\upsilon}{k_BT}}$$

$$C_V = \frac{dU}{dT} = -3N_A h\upsilon\left[-e^{-\frac{h\upsilon}{k_BT}}\left(\frac{h\upsilon}{k_BT^2}\right)\right]$$

$$3N_A k\left[\frac{h\upsilon}{k_BT}\right]^2 e^{-\frac{h\upsilon}{k_BT}} = 3R\left(\frac{h\upsilon}{k_BT}\right)^2 \exp\left(-\frac{h\upsilon}{k_BT}\right) \quad \text{... (v)}$$

Equation (v) indicates that at low temperature the exponential term is more important than the $\left(\frac{h\upsilon}{k_BT}\right)^2$ term in determining the temperature variation of C_V

Thus with decreasing temperature C_V drops exponentially

$$C_V = 3R\left(\frac{h\upsilon}{k_BT}\right)^2\left[1+\frac{h\upsilon}{k_BT}+\frac{1}{21}\left(\frac{h\upsilon}{k_BT}\right)^2+.....\right]$$

As $T \rightarrow 0$ $C_V = 0$

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Atomic specific heat of different element differs only because of characterstic frequency υ. At correspondng temp such that $\frac{\upsilon}{T}$ are same of the atomic specific heat will be same for different element. Eienstein theory is in good agreement with the experimental but in case of some solids it is observed that atomic specific heat at low temp decreases more slowly than predicted by this theory.

Q. 84. What is law of equipartition of energy ? Derive this using Maxwell's distribution law of molecular velocity.

Ans. This law is applicable to a system of particles in equilibrium and states that average K.E per particle per degree of freedom is $\frac{1}{2}k_BT$ where k_B- Boltzmann's const T $\rightarrow$ absolute temperature.

Derivation : Maxwell's distribution law

$$dN(\bar{C}) = N\left(\frac{m}{2\pi m k_B T}\right)^{3/2} e^{-m\left(C_x^2 + C_y^2 + C_z^2\right)/2k_BT} dc_x\, dc_y\, dc_z$$

Where N is the total no. of molecule in the gas and C_x C_y C_z are the velocity components. Since each of the three components must have the same velocity distribution, the no. of molecules with velocity component between C_x & $C_x + dC_x$ irrespective of other component is

$$dN(C_x) = N\left(\frac{m}{2\pi m k_B T}\right)^{1/2} e^{-mC_x^2/2k_BT} dC_x$$

The average K.E of a molecule in the x-direction

$$\bar{E}_x = \frac{1}{N}\int \left(\tfrac{1}{2}mC_x^2\right) dN(C_x)$$

$$= \frac{1}{2}m\left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^\infty e^{-bC_x^2} C_x^2\, dx$$

Put $\frac{m}{2k_BT} = b$

$$= \int_{-\infty}^{\infty} e^{-\alpha x^2} x^2\, dx = \frac{1}{2b}\sqrt{\frac{\pi}{b}}$$

Therefore $E_x = \frac{m}{4b} = \frac{1}{2}k_BT$

Similarly $\bar{E}_y = \bar{E}_z = \frac{1}{2}k_BT$

This is valid for each degree of freedom. Each molecule of an ideal gas has three translational drgree of freedom and so the average K.E per molecule is $\frac{3}{2}k_BT$.

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Q. 85. What is law of equipartition of energy? Use this to show that mean energy of a classical simple harmonic oscillator is k_BT. Also state the limitation of this law?

Ans. This law states that if a classical system is in thermal equilibrium at absolute temp T then every independent quadratic term in its energy has a mean value equal to $\frac{1}{2}k_BT$.

For a simple harmonic oscillator

$$F = \frac{p^2}{2m} + \frac{1}{2}kx^2 \qquad ...(1)$$

where k- Force constant

$E = K.E + P.E$

Suppose that this oscillator is in equilibrium with a heat reservoir at a temperature T which is very high. So mean energy of the oscillator is

$$\bar{E} = \frac{\int E\, e^{-\beta E} dx dp_x}{\int e^{-\beta E} dx dp_x} - (2) \quad \beta = \frac{1}{k_B T}$$

Using eqn (1) in eqn(2)

$$\bar{E} = \frac{\int \frac{p_x^2}{2m} e^{\frac{-\beta p_x^2}{2m}} dp_x}{\int e^{\frac{-\beta p_x^2}{2m}} dp_x} + \frac{\int \frac{1}{2} kx^2 e^{\frac{-\beta k x^2}{2}} dx}{\int e^{\frac{-\beta k x^2}{2}} dx}$$

$$= -\frac{d}{d\beta} \log_e \left[\int_{-\infty}^{\infty} e^{\frac{-\beta p_x^2}{2m}} dp_x \right] - \frac{\partial}{\partial \beta} \log \left[\int_{-\infty}^{\infty} e^{\frac{-\beta k x^2}{2}} dx \right]$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \left[-\frac{1}{2} \log \beta + \log \int_{-\infty}^{\infty} e^{\frac{-A^2}{2m}} dA \right] - \frac{\partial}{\partial \beta} \left[\frac{1}{2} \log \beta + \log \int_{-\infty}^{\infty} e^{\frac{\beta k x^2}{2}} d\beta \right]$$

where $A = \sqrt{\beta} P_x$ and $A = \sqrt{\beta} x$

But $\int_{-\infty}^{\infty} e^{-A^2/2m}\, dA = 0 = \int_{-\infty}^{\infty} e^{-\beta^2/2m}\, dB$

So $\bar{E} = \frac{-\partial}{\partial \beta}\left[-\frac{1}{2} \log \beta \right] \frac{-\partial}{\partial \beta} \frac{1}{2} \log \beta$

$$= \frac{1}{2\beta} + \frac{1}{2\beta} = k_B T$$

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Q. 86. The equation of state of an ideal gas is given by PV = RT. Show that

$$\beta = \frac{1}{T} \quad \text{and} \quad Z = \frac{1}{P}$$

(ii) An approximate equation of state of a real gas at moderate pressure is P(V – b) = RT. Where R and b are constant. Show that

$$\beta = \frac{\frac{1}{T}}{1 + \frac{Pb}{RT}} \qquad \text{(ii)} \quad Z = \frac{\frac{1}{P}}{\frac{1+Pb}{RT}}, \quad Z = \text{Compressibility}$$

Ans. β for an ideal gas is defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right) \qquad ... (1)$$

The eqn of state is $PV = RT$

$$\frac{\partial V}{\partial T} = \frac{R}{P} \quad \text{and} \quad R = \frac{PV}{T}$$

Substituting these value in eqn (1)

$$\beta = \frac{1}{V}.\frac{1}{P} \times \frac{PV}{T} \quad \Rightarrow \quad \beta = \frac{1}{T}$$

(ii) For an ideal gas compressibility $Z = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$PV = RT \Rightarrow \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

So $$Z = -\frac{1}{V} \times -\frac{RT}{P^2} \Rightarrow \frac{RT}{P^2V} = \frac{PV}{P^2V} = \frac{1}{P} \Rightarrow Z = \frac{1}{P}$$

$$P(V-b) = RT$$

$$V = \frac{RT}{P} + b$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{P}{Pb + RT} \cdot \frac{R}{P} \Rightarrow \beta = \frac{R}{Pb + RT}$$

Now, $$\beta = \frac{\frac{RT}{T}}{RT\left(1 + \frac{Pb}{RT}\right)} = \frac{RT}{T} \times \frac{1}{RT\left(1 + \frac{Pb}{RT}\right)} \Rightarrow \boxed{\beta = \frac{\frac{1}{T}}{1 + \frac{Pb}{RT}}}$$

$$P(V-b) = RT \Rightarrow V = \frac{RT}{P} + b$$

$$\Rightarrow \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

Now, $$Z = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V}\left(-\frac{RT}{P^2}\right)$$

$$Z = \frac{P}{RT + Pb} \cdot \frac{RT}{P^2} = \frac{RT}{P(RT + Pb)}$$

$$\boxed{Z = \frac{\frac{1}{P}}{1 + \frac{Pb}{RT}}}$$

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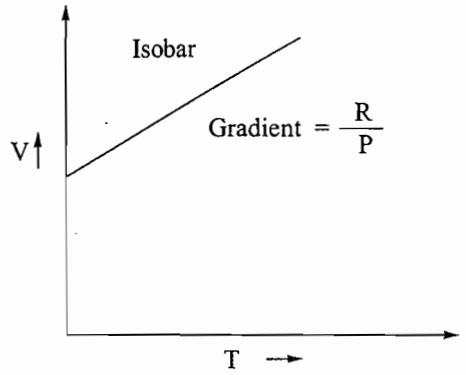
Q. 87. A gas obeys the equation of state P(V – b) = RT where b is a constant for this gas sketch
(i) a Plot of V versus T at constant P (isobar)
(ii) a plot of P versus V at constant T (isotherm)
(iii) a plot of P versus T at constant V (isochore)

Ans. P = constant then the equation of state P(V– b) = RT can be written

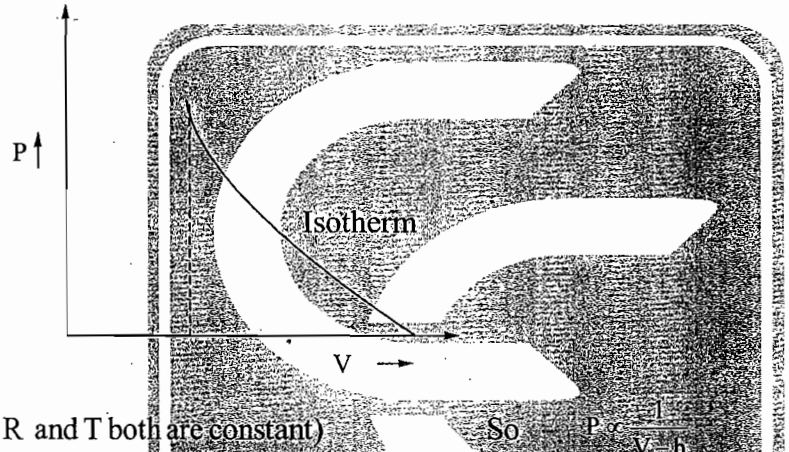
$$V = \frac{RT}{P} + b \quad \frac{RT}{P} \quad \frac{RT}{P}$$



This shows that when $T = 0$ $V = b$. Then the plot of V versus T is a straight line with gradient $\frac{R}{P}$ and intercept b as shown in fig.

(ii) If T is constant (isotherm) the eqn of state can be written

$$P = \frac{RT}{V-b} = \frac{const}{V-b}$$



(Since R and T both are constant) So $P \propto \frac{1}{V-b}$

It can easily seen that when $V \to \infty$, $P \to 0$ and when $V \to b$, $P \to \infty$. Thus the curve is as shown in fig.

(iii) If V is constant (Isochore) $\Rightarrow P = \frac{RT}{V-b} = \frac{RT}{const}$

(since V and b are const)

when $T = 0 \Rightarrow P = 0$

$V = b \Rightarrow P = \infty$

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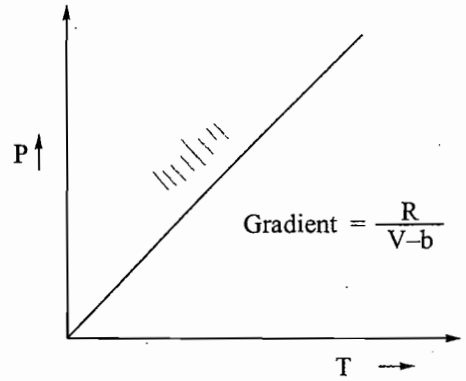

So the plot of P versus T is a straight line with gradient $\frac{R}{V-b}$ and zero intercept as shown.

Q. 88. What is Einstein quantum theory of specific heat? Discuss its limitation.

Ans. Einstein applied Planck's quantum theory to specific heats of solids. In this the average energy of an oscillator per degree of freedom is

$$U = E = \frac{h\upsilon}{e^{h\upsilon/k_BT}-1}$$ for N atoms that will be 3N degree of freedom

Hence $$U = E = \frac{3Nh\upsilon}{e^{h\upsilon/k_BT}-1}$$

and molar specific heat $$C_V = \frac{dU}{dT} = -\frac{3Nh\upsilon\, e^{h\upsilon/k_BT}\left(-h\upsilon/k_BT^2\right)}{\left(e^{h\upsilon/k_BT}-1\right)^2}$$

$$C_V = \frac{3NKe^{h\upsilon/k_BT}\left(\frac{h\upsilon}{k_BT}\right)^2}{\left(e^{h\upsilon/k_BT}-1\right)^2} = 3R\left(h\upsilon/k_BT\right)^2\frac{e^{h\upsilon/k_BT}}{\left(e^{h\upsilon/k_BT}-1\right)^2}$$

If $\frac{h\upsilon}{k_B} = \theta_E$, $C_V = 3R\left(\frac{\theta_E}{T}\right)^2\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T}-1\right)^2}$ ...(1)

where $\theta_E = \frac{h\upsilon}{k_B}$ is known as Einstein's Characterstic temperature

Case-1 : At high temp $T >> \theta_E$

we have $\frac{\theta_E}{T} << 1$ so that $e^{\theta_E/T} = 1 + \frac{\theta_E}{T}$

so eq^n (1) become $C_V = 3R$ ...(2)

This is in agreement with Dulong Petit's law

Case-2: At low temp $T << \theta_E$

we have $\frac{\theta_E}{T} >> 1$ so that $e^{\theta_E/T} >> 1$

so eqn (1) become

$$C_V = 3R\left(\frac{\theta_E}{T}\right)e^{-\theta_E/T}$$ ... (3)

This show that as $T \to 0$ the specific heat C_V also approach to zero

Limitation :- The theory fails at very low temp where C_V is found to be nearly proportional to T^3 rather than as given by eqn (3). This is due to neglecting the mutual forces exerted by the atom upon one another.

Q. 89. Show that if f is the Fermi-Dirac distribution function is a maximum at the fermi level, Also show that $-\frac{\partial f}{\partial E}$ is symmetric about the Fermi-level.

Ans. We have $f = \frac{1}{1+e^{\frac{E-E_F}{k_BT}}} = \frac{1}{1+e^x}$ where, $x = \frac{E-E_F}{k_BT}$, $E_F \to$ Fermi level

Now $\frac{\partial f}{\partial E} = \frac{\partial f}{\partial x}\cdot\frac{\partial x}{\partial E} = -\frac{e^x}{(\quad)^2}\cdot\frac{1}{k_BT}$ $-\frac{\partial f}{\partial E} = \frac{1}{k_BT}\frac{e^x}{(\quad)^2}$

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and $$-\frac{\partial^2 f}{\partial E} = -\frac{d}{dx}\left[\left(\frac{\partial f}{\partial E}\right)\frac{\partial x}{\partial E}\right] = \frac{1}{k_B T}\frac{d}{dx}\left(-\frac{\partial f}{\partial E}\right) = \frac{1}{(k_B T)^2}\frac{\left(1+e^x\right)^2 e^x - 2e^x\left(1+e^x\right)e^x}{\left(1+e^x\right)^4}$$

$-\frac{\partial f}{\partial E}$ is a maximum when $-\frac{\partial^2 f}{\partial E^2} = 0$

$$\left(1+e^x\right)^2 - 2e^x\left(1+e^x\right) = 0$$
$$\left(1+e^x\right)\left[1+e^x-2e^x\right] = 0$$
$$\left(1+e^x\right)\left(1-e^x\right) = 0$$
$$1-e^{2x} = 0$$
$$e^{2x} = 1 = e^o \Rightarrow x = 0$$
$$x = \frac{E-E_F}{k_B T} = 0 \Rightarrow E = E_F$$

Thus $-\frac{\partial f}{\partial E}$ is a maximum at the fermi level

If E is below E_F by the same amount, x is replaced by (–x)

Then $-\frac{\partial f}{\partial E} = \frac{1}{k_B T}\frac{e^{-x}}{\left(1+e^{-x}\right)^2} = \frac{1}{k_B T}\frac{e^x}{\left(1+e^x\right)^2}$

$$\left(\frac{e^{-x}}{\left(1+e^{-x}\right)^2} = \frac{e^{2x}\times e^{-x}}{e^{2x}\left(1+e^{-2x}+2e^{-x}\right)} = \frac{e^x}{e^{2x}+1+2e^x} = \frac{e^x}{\left(1+e^x\right)^2}\right)$$

Thus $-\frac{\partial f}{\partial E}$ is unchanged upon the reversal of the sign of x

Hence $-\frac{\partial f}{\partial E}$ is symmetric about x = 0 i.e about $E = E_F$

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Q. 90. By considering the variation of E_F with volume show that there is a relation between pressure and volume of the free electron gas as PV = 2/3 U, where U is the internal energy of the gas at zero Kelvin. Hence show that the isothermal elasticity of the electron gas is β = 9V/10U free particle is represented by a plane wave e^{ikx}.

Ans. The general expression for energy is $U = \frac{\hbar^2 K^2}{2m} \rightarrow$ energy of free particle with Kr = constant (say α)

Volume $V = br^3$ with b = constant = $\frac{4}{3}\pi$

Thus $$= U = \frac{\hbar^2}{2m}\left(\frac{\alpha^2}{r^2}\right) = \frac{\hbar^2\alpha^2}{2m}\left(\frac{b}{V}\right)^{2/3} \quad \ldots (1)$$

Differentiating equation (1) w.r.t V we get

$$\frac{dU}{dV} = \frac{\hbar^2\alpha^2}{2m} b^{2/3}\left(\frac{-2}{3}\frac{1}{V^{5/3}}\right)$$

we know that, $P = -\left(\frac{dU}{dV}\right)$ ... (2)

Thus, $P = \frac{\hbar^2\alpha^2}{2m} b^{2/3} \frac{2}{3} \left(\frac{1}{V^{2/3}}\right)\left(\frac{1}{V}\right)$

So $PV = \frac{\hbar^2\alpha^2 b^{2/3}}{2m} \frac{2}{3} \frac{1}{V^{2/3}} = \frac{2}{3}\frac{\hbar^2\alpha^2}{2m}\left(\frac{b}{V}\right)^{2/3}$

$$\boxed{PV = \frac{2}{3}U}$$ ... (3)

Now differentiating equation (3) we get

$$P + V\left(\frac{dP}{dV}\right) = \frac{2}{3}\frac{dU}{dV}$$

Using equation (2)

$$P + V\left(\frac{dP}{dV}\right) = \frac{2}{3} x \left(-P\right)$$

$$V\frac{dP}{dV} = -\frac{5}{3}P \Rightarrow \frac{dV}{VdP} = \frac{3}{5P}$$

Isothermal elasticity $B = \frac{1}{V\left(\frac{\partial V}{\partial P}\right)}$

$$B = \frac{3}{5P}$$

From eqn 3 $P = \frac{2}{3}\frac{U}{V}$ $\Rightarrow \frac{1}{P} = \frac{3V}{2U}$

So $B = \frac{3}{5} \times \frac{3V}{2U} = \frac{9V}{10U}$

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Q. 91. In a system of two particles each particle can be in any one of three possible quantum state. Find the ratio of the probability that the two particles occupy the same state to the probability that the two particles occoupy different states for MB, BE and ED statistics

Ans. Let r be the desired ratio

$W_1 \rightarrow$ the number of ways in which two particles can occupy same state

$W_2 \rightarrow$ The state in which they occupy different state then

$$r = \frac{W_1}{W_2}$$

For MB Statistics :

The particles are distinguishable and $W_1 = 3$

Now one particle can be in any one of the 3 quantum state and remaining particles can be in any one of the 2 quantum state that are available to it. So

$$W_2 = 3 \times 2 = 6$$

Therefore $r = \frac{W_1}{W_2} = \frac{3}{6} = \frac{1}{2}$

For FD statistics :

The particles are indistinguishable, $W_1 = 0$. Since the two particles can't be in the same quantum state

Here $W_2 = {}^3C_2 = 3$

So $r = \frac{W_1}{W_2} = \frac{0}{3} = 0$

For BE statistics : Again the particles are indistinguishable

$W_1 = 3$ and $W_2 = 3_{C_2} = 3$

So $r = \frac{W_1}{W_2} = \frac{3}{3} = 1$

Q. 92. Show that for a two dimensional electron gas the number of electrons per unit area is given by

$$n = \frac{4\pi m k_B T}{h^2} \ell n\left(e^{\frac{E_F}{k_B T}} + 1\right)$$

Ans. The density of state function for a two dimensional electron gas is given by

$$g(E)dE = \frac{2A}{h^2}(2\pi p dp) = \frac{4\pi m A}{h^2} dE$$

$$\left(\because E = \frac{p^2}{2m} \Rightarrow p^2 = 2mE \quad \text{so} \quad 2pdp = 2mdE\right)$$

$A \rightarrow$ Area of two dimensional container, $m =$ mass of electron

The number of electron is

$$N = \int_o^\infty g(E) f(E) dE = \frac{4\pi m A}{h^2} \int_o^\infty \frac{dE}{1 + e^{\frac{E - E_F}{k_B T}}}$$

The number of electrons per unit area is given by

$$n = \frac{N}{A} = \frac{4\pi m k_B T}{h^2} \int_o^\infty \frac{dx}{1 + e^{x - \eta}}$$

where $x = \frac{E}{k_B T} \Rightarrow dx = \frac{dE}{k_B T}$ and $\eta = \frac{E_F}{k_B T}$

Now the integral $I = \int_o^\infty \frac{dx}{1 + e^{x-\eta}} = \int_o^\infty \frac{e^{-x} dx}{e^{-x} + e^{-\eta}}$

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Substituting $Z = e^{-x} + e^{-\eta} \Rightarrow dZ = -e^{-x}dx$

$$\text{So } I = \int_{e^{-\eta}}^{1+e^{-\eta}} \frac{dZ}{Z} = \ell n \left(\frac{1+e^{-\eta}}{e^{-\eta}}\right) = \ell n \left(1+e^{+\eta}\right)$$

$$\text{So } n = \frac{4\pi m k_B T}{h^2} \ell n \left(1+e^{E_F/k_B T}\right)$$

Q. 93. The earth receives 2.0 cal cm^{-2} min^{-1} from the sun. If angular diameter of the sun is 32' and is treated as a black body, deduce its surface temperature.

Given: $\sigma = 5.7\times10^{-12}$ watt cm^{-2} K^{-4} ?

Soln. As $T^4 = \frac{S}{\sigma}\left(\frac{R}{r}\right)^2$

Solar constant $S = \frac{2}{60}$ cal cm^{-2} min^{-1}

$$= \frac{2\times4.2}{60} \text{ joule} \times \left(10^{-2}\text{ m}\right)^{-2} \times \text{min}^{-1}$$

$$= 14\times10^2 \text{ joule } m^{-2} \text{ } min^{-1}$$

$$\left(\frac{r}{R}\right) = \frac{\text{radius of the sun}}{\text{distance of the earth from the sun}}$$

Angular diameter = 32'

$$\text{angular radius} = \frac{r}{R} = \frac{32'}{2} = 16' = \left(\frac{16}{60}\right)^0$$

$$= \frac{16}{60}\frac{\pi}{180} \text{ radian}$$

$$\frac{R}{r} = \frac{180\times60}{16\times\pi}$$

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Thus $T^4 = \frac{14\times10^2}{\sigma}\times\left(\frac{180\times60}{16\pi}\right)^2$

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$$= \frac{14\times10^2}{5.7\times10^{-8}}\times\left(\frac{180\times60}{16\pi}\right)^2$$

$\sigma = 5.7\times10^{-12}$ watt $cm^{-2}K^{-4}$

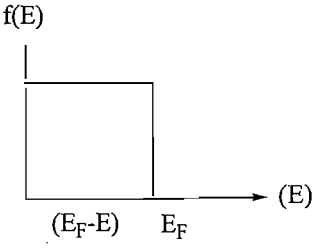
$= 5.7\times10^{-8}$ watt $m^{-2}K^{-4}$

$\Rightarrow$ $\boxed{T = 5803K}$

Q. 94. Show that a fraction of $\bar{e}$ in free $\bar{e}$ gas at T = 0K between $(E_F - E)$ and $E_{F(\epsilon<<E_F)}$ is $\frac{3\epsilon}{2E_F}$?

Soln. $N = \int_0^{E_F} g(E)f(E)dE$

Since $g(p)dp = \frac{4\pi V}{h^3}p^2dp$



$$g(E)dE = \frac{4\pi V}{h^3}.p^2.\frac{m}{p}dE$$

$$= \frac{4\pi V}{h^3}\left(\sqrt{2mE}\right).mdE \qquad \left[\begin{array}{l} \text{As } p^2 = 2mE \\ \Rightarrow 2pdp = 2mdE \\ \Rightarrow dp = \frac{m}{p}dE \end{array}\right]$$

$$= \frac{2\pi V}{h^3}(2m)^{3/2}E^{1/2}dE$$

$$= AE^{1/2}dE$$

$$N = A\int_0^{E_F} E^{1/2}dE = A.\frac{2}{3}E_F^{3/2}$$

No. density of states upto $E_F - \epsilon$

$$N' = A\int_0^{E_F-\epsilon} E^{1/2}dE = A\frac{2}{3}(E_F-\epsilon)^{3/2}$$

$$\text{fraction of } \bar{e} = \frac{N-N'}{N} = \frac{E_F^{3/2}-(E_F-\epsilon)^{3/2}}{(E_F)^{3/2}} = \frac{E_F^{3/2}-E_F^{3/2}\left(1-\frac{\epsilon}{E_F}\right)^{3/2}}{(E_F)^{3/2}} = 1-\left(1-\frac{3}{2}\frac{\epsilon}{E_F}\right)$$

$$\Rightarrow \boxed{\frac{N-N'}{N} = \frac{3}{2}\frac{\epsilon}{E_F}}$$

Q. 95. N particles obey M.B statistics are distributed among three states having energy $\epsilon_1 = 0, \epsilon_2 = k_BT$ and $\epsilon_3 = 2k_BT$. If total equilibrium energy of the system is 1000 k_BT. What is value of N?

Soln. Since **number of particles** **energy**

$$N_1 + N_2 + N_3 = N \qquad N_3 \xrightarrow{\text{(iii)}} 2k_BT$$

$$\text{Now } \frac{N_1}{N_2} = \frac{e^{-\beta\epsilon_1}}{e^{-\beta\epsilon_2}} \qquad N_2 \xrightarrow{\text{(ii)}} k_BT$$

$$N_1 \xrightarrow{\text{(i)state}} 0$$

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$$\Rightarrow \qquad N_1 = N_2\, e^{-\beta(\epsilon_1-\epsilon_2)} \qquad \ldots (1)$$

Similarly $\qquad N_2 = N_3\, e^{-\beta(\epsilon_2-\epsilon_3)} \qquad \ldots (2)$

from (1) $N_1 = N_2\, e^{-\frac{(0-k_BT)}{k_BT}} = N_2 e \quad , \quad \left\{\beta = \frac{1}{k_BT}\right.$

$$N_3 = N_2\, e^{+\frac{(k_BT)-2k_BT)}{k_BT}}$$

$$= N_2\, e^{-1}$$

Thus $N = N_1 + N_2 + N_3$

$= N_2\, e + N_2 + N_2\, e^{-1}$

$= N_2 \left(e + 1 + \frac{1}{e} \right)$ ... (3)

As $1000\, k_B T = 0 + k_B T\, N_2 + 2k_B T\, N_3$

$\Rightarrow \quad 1000 = N_2 + 2N_2 e^{-1}$ ... (4)

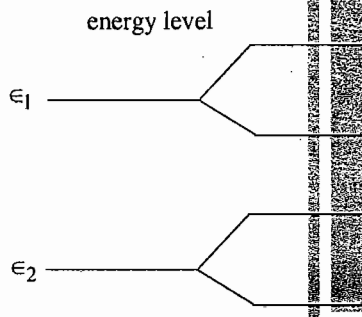
from (3) and (4)

$$\frac{N}{1000} = \frac{e + 1 + e^{-1}}{1 + 2e^{-1}} = 2.354$$

$$= N = 2354 \approx 2400$$

Q. 96. Four identical fermions are to be distributed in energy level ϵ_2 is 6 fold degenerate. Find the energy corresponding to the distribution having maximum number of arrangement.

Soln. The no. of ways in which particles can be distributed is
$(4, 0), (0, 4), (1, 3), (3, 1), (2, 2)$



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Total no. of ways $\Omega = \left(\frac{(g_i}{(n_i (g_i - n_i} \times \frac{(g_i}{(n_i (g_i - n_i} \right)$

$$\Omega_{4,0} = \frac{(5}{(4(5-4} \times \frac{(6}{(o\,(6} = 5$$

$$\Omega_{0,4} = \frac{(5}{(0(5} \times \frac{(6}{(4\,(6-4} = 15$$

$$\Omega_{3,1} = \frac{(5}{(3(2} \times \frac{(6}{(1\,(5} = 60$$

$$\Omega_{1,3} = \frac{(5}{(1(4} \times \frac{(6}{(3\,(3} = 100$$

$$\Omega_{2,2} = \frac{(5}{(2(3} \times \frac{(6}{(2\,(4} = 150$$

Energy having maximum no. of arrangements $= 2\epsilon_1 + 2\epsilon_2$

References

The following books have been referred to while preparing this booklet. The authors of this booklet owe credits to all of them.

Heat and Thermodynamics	–	**M.W. Zemansky, R.H. Dittman**
Fundamentals of Statistical & Thermal Physics	–	**F. Rief**
An introductory course of Statistical Mechanics	–	**Palash B Pal**
Statistical & Thermal Physics An Introduction	–	**S. Lokanathan, R.S. Gambhir**
Statistical Mechanics	–	**R.K. Patharia**

For the students interest, they can refer to the following books for further reading.

Statistical Mechanics	–	**Kerson Huang**
Thermal Physics	–	**Charles Kittel**
A Treatise on Heat	–	**Saha & Srivastava**
Engineering Thermodynamics	–	**P.K. Nag**
Thermodynamics	–	**Garg, Bansal & Ghosh**
Heat & Thermodynamics	–	**H.P. Roy & A.B. Gupta**
Heat Thermodynamics & Statistical Physics	–	**Brijlal & Subramanyam**

The image on the Front Cover a 3D graph of Bose-Einstein Condensate obtained by a group headed by Carl Wieman and Eric Cornell. We owe the credits to them.